INDIAN AGRICULTURAL RESEARCH INSTITUTE (PUSA)

IARI

LIBRARY
New Delhi

Call No _____

Acc No 67487

Indian Agricultural Research Institute (Pusa)
LIBRARY, NEW DELHI-110012

This book can be issued on or after _____

Return Date	Return Date

4 Unless a borrower points out the injury at the time of borrowing the book, he shall be required to replace the book or pay its price if detected at the time of return.

HELP US TO KEEP THIS BOOK FRESH AND CLEAN

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1947-49

L67|9

PART 1] SECTION A [VOL. 16

CONTENTS

PAGE

Study of the Complex Formation Between Mercuric Chloride and Soluble Chlorides by the Electrical Conductivity Method

By Arun K. Dey and A. K. Bhattacharya 1

Fixation and Loss of Nitrogen and the Source of Soil Nitrogen

By N. R. Dhar 6

Oxidation of Edible Substances by Hydrogen Peroxide With Iron as Catalyst

By N. R. Dhar and B V. S. Raghavan 14

Investigations on Nickel Ammines

By C. S. Shaw and S Ghosh 20

Studies in the Production of Yeast

By N. R. Dhar and Krishna Bahadur 24

Quantitative Study of the Extent of Inhibition of the Precipitation of Stannic Sulphide in Presence of Soluble Tartrates

By Arun K. Dey 27

Studies in the Dyes Derived from Quinolinic Acid and Cinchomeronic Acid as Adsorption Indicators in Argentometric Titrations:

By R. C. Mehrotra 31

67487

IARI

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India): Rs 5/8 (Foreign)

67487

INSTRUCTIONS TO CONTRIBUTORS

Articles should be as *brief* as possible. The viewpoint should be comprehensive in giving the relation of the paper to previous publications of the author or of others and in exhibiting, when practicable, the significance of the work for other branches of science. Elaborate technical details of the work and long tab s of data should be avoided, but authors should be precise in making clear the n v results and should give some record of the methods and data upon which they are based.

Manuscripts should be prepared with a current number of the PROCEEDINGS as a model in matters of form, and should be type-written in duplicate with double spacing, the author retaining one copy. Illustrations should be confined to text-figures of simple character, though more elaborate illustrations may be allowed in special instances to authors willing to pay for their preparation and insertion. Authors are requested to send in all drawings or other illustrations in a state suitable for direct photographic reproduction. They should be drawn on a large scale in Indian Ink on Bristol board, with temporary lettering in pencil. Great care should be exercised in selecting only those that are essential. If unsatisfactory drawings are submitted, authors may be required to have them redrawn by a professional artist. Particular attention should be given to arranging tabular matter in a simple and concise manner.

References to literature will be placed at the end of the article and short footnotes should be avoided. It is suggested that references to periodicals be furnished in some details and in general in accordance with the standard adopted for the Subject Catalogue of the International Catalogue of Scientific Literature, *viz.*, name of author, arranged alphabetically, with initials following (ordinarily omitting title of paper), year, abbreviated name of Journal, volume, inclusive pages.

Papers by members of the Academy may be sent to the General Secretary, National Academy of Sciences, Allahabad. Papers by non-members of the Academy should be submitted through a member.

No Papers exceeding twelve pages of printed matter will be published in the PROCEEDINGS except with a special permission of the Council.

Every paper must be accompanied by *three copies* of a brief summary not exceeding 300 words in length.

A Proof will ordinarily be sent and the author is requested to return it with the manuscript, at his earliest convenience. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1947

PART II] SECTION A [VOL. 16

CONTENTS

Page

1. Study of the preparation and properties of Argento-thiosulphate Complexes and determination of the valency of the complex radical by coagulation experiments.

By Arun K. Dey & S. P. Mushran 37

2. Thermal ionization of Calcium and determination of specifc charge of Ca^{+}.

By A. S. Bhatnagar 45

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES INDIA
1947

PART III] SECTION A [VOL. 16

CONTENTS

PAGE

Thermal Ionization of Aluminium and Determination of the Specific Charges of Al^+

By A. S. Bhatnagar 53

Study of the Complex Formation between Mercuric Chloride and Soluble Chlorides by the Electrical Conductivity method (Part II—Study of the $HgCl_2$—KCl System)

By Arun K. Dey 61

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

ERRATA

'On page 18 in Table 3 read 13 3 and 4 32 instead of 3 3 and 43 2'

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES

INDIA

(SECTION A)

Part 1] 1947 [V] c 1(

STUDY OF THE COMPLEX FORMATION BETWEEN MERCURIC CHLORIDE AND SOLUBLE CHLORIDES BY THE ELECTRICAL CONDUCTIVITY METHOD

Part I Complex Chloromercuric Acids

By ARUN K DEY AND A K BHATTACHARYA

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SALCAR

(Received on 26th April 1947)

ABSTRACT

The complex formation between mercuric chloride and hydrochloric acid has been investigated by the electrical conductivity method It has been concluded that the complex compounds, HCl, $HgCl_2$, 2HCl, $HgCl_2$ and 4HCl, $HgCl_2$ exist in solution

The enhanced solubility of mercuric chloride in presence of hydrochloric acid was noted by Rose[1] and later Le Blanc and Noyes[2] inferred the formation of complex ions in solution Various workers, notably Ditte[3] and Sherrill[4] studied the composition of these complexes Numerous workers have tried the isolation and analysis of the complex compounds, but the results obtained are still not convincing In recent years, Krishnamurti[5], Braune and Englebrecht[6], and Bernstein and Martin[7] have adopted physico chemical methods for the study of the composition of the complexes formed in solution, and their results together with those obtained by Nayar and Saraf[8] lead us to believe that in all cases $HHgCl_3$ is formed in the solution

In this paper, we have studied this problem from electric conductivity measurements

EXPERIMENTAL

The electrical conductivity for an M/100 mercuric chloride solution diluted with an equal volume of water was 6.343×10^{-6} mhos at 30°

The electrical conductivity of hydrochloric acid solutions of different concentrations were determined The results are tabulated below

TABLE I

Temperature 30°

Concentration of hydrochloric acid solution	Electrical conductivity in 10^{-3} mhos
M/10	37.88
M/20	19.78
M/30	13.14
M/40	9.79
M/45	8.600
M/50	7.564
M/60	6.584
M/70	5.619
M/80	4.866
M/90	4.362
M/100	3.937
M/110	3.670
M/120	3.289
M/130	2.966
M/140	2.880
M/150	2.646
M/160	2.495
M/180	2.120
M/200	2.064
M/240	1.642
M/280	1.369

TABLE II

Temperature 30°

Final concentrations of the constituents in the mixture		Ratio		Electrical conductivity in 10^{-3} mhos
$HgCl_2$	HCl	$HgCl_2$	HCl	
M/200	M/10	1	20 0	37 904
,,	M/20	1	10 0	19 884
,,	M/30	1	6 67	13 224
,,	M/40	1	5 00	9 989
,	M/45	1	4 44	8 921
,,	M/50	1	4 00	8 120
,	M/60	1	3 33	6 600
,,	M/70	1	2 86	5 651
,,	M/80	1	2 50	4 925
,,	M/90	1	2 22	4 606
,,	M/100	1	2·00	4 185
,,	M/110	1	1 82	3 735
,,	M/120	1	1 67	3 355
,,	M/130	1	1 54	3 012
,,	M/140	1	1 43	2 937
,,	M/150	1	1 33	2 703
,,	M/160	1	1 25	2 589
,,	M/180	1	1 11	2 202
,,	M/200	1	1 00	2 173
,,	M/240	1	0 83	1 670
,,	M/280	1	0 71	1 393

DISCUSSION

The electrical conductivity of the mixture in a complex forming system depends on the number of ions formed by complex formation, and also on the respective ionic mobilities of the new ions Any deviation from the additive values may be ascribed to be due to the complex formation. With this criterion, we have in the following table calculated the percentage change in electrical conductivities of mixtures of mercuric chloride and hydrogen chloride of various compositions, due to the formation of complex ions,

TABLE III

Composition of the mixture $HgCl_2$: HCl	Sum of the conductivities of the constituents in 10^{-3} mhos.	Observed conductivity of the mixture in 10^{-3} mhos.	Difference in 10^{-4} mhos.	Percentage difference.
1 : 20·0	37·88	37·904	1·04	0·28
1 : 10·0	19·78	19·884	1·04	0·53
1 : 6·67	13·14	13·224	1·84	1·40
1 : 5·00	9·799	9 989	1 90	1·94
1 : 4·24	8·606	8·921	3·15	3·66
1 : 4 00	7·670	8 120	4·50	5·86
1 : 3·33	6·390	6·600	2·10	3·28
1 : 2·86	5·615	5·651	0·36	0·64
1 : 2·50	4·872	4·923	0·51	1·04
1 : 2·22	4·368	4·606	2·38	5·45
1 : 2·00	3·943	4·185	2 42	6·14
1 : 1·82	3·676	3·735	0·59	1·60
1 : 1·67	3·305	3·355	0·50	1·51
1 : 1·54	2·972	3 012	0·40	1·34
1 : 1·42	2·885	2·937	0·51	1·76
1 : 1·33	2·652	2 703	0 61	1·92
1 : 1·25	2·501	2·589	0·88	3·52
1 : 1·11	2·126	2·202	0·76	3·57
1 : 1·00	2·070	2 173	1 03	4·97
1 : 0·83	1 648	1·670	0·22	1·33
1 : 0·71	1 375	1·393	0·18	1·30

From the results given in table IV, we have plotted a graph showing the change of percentage difference with composition of the mixture. It is seen from the graph that the maxima points correspond to the following ratios of $HgCl_2$: HCl – 1 : 1 ; 1 : 2 and 1 : 4. Thus we have evidence of the complex compounds, $HgCl_2$, HCl; $HgCl_2$, 2HCl and $HgCl_2$, 4HCl in the solution.

We therefore conclude, that the compounds formed by the complex formation between mercuric chloride and hydrogen chloride are different in composition, depending on the concentrations of the constituents.

References

1 Rose *Pogg Ann*, 1837, **40** 75

2 Le Blanc and Noyes *Zeit Phys Chem*, 1890, **6**, 401

3 Ditte *Ann Chem Phys*, 1881 (5), **22**, 551
Compt Rend, 1880, **91** 986

4 Sherill *Zeit. Phys Chem*, 1903, **43**, 705

5 Krishnamurti *Indian J Phys*, 1931 **6**, 7

6 Braune and Fnglebrecht *Zeit Phys Chem*, 1930, **11B**, 409

7 Bernstein and Martin *Trans Roy Soc, Canada*, 1937, **34**, 111 95

8 Naya and Sarif *J Ind Chem Soc*, 1943, **20**, 314

FIXATION AND LOSS OF NITROGEN AND THE SOURCE OF SOIL NITROGEN

By N. R. Dhar

(*Read on 15th September*, 1947)

Russell[1] has reported that the nitrogen content of the soil in wheat plot 2 B in Rothamsted in 1865 was 0.196% *i.e.* 4850 lbs. of nitrogen per acre and in 1914 the total nitrogen went up to 0.236% *i.e.* 5590 lbs. total nitrogen per acre when farmyard manure at the rate of 14 tons containing 200 lbs. of nitrogen were added per acre. From our experiments with cowdung we find that the ratio of C : N is 20 or 21 : 1. Assuming 20 : 1 as the C : N ratio of farmyard manure in Rothamsted, the amount of carbon introduced in Rothamsted is approximately 4000 lbs. per acre. Our experimental results with nitrogen fixation using cowdung as the energy material show that when the total nitrogen content of the system is 0.180%, the efficiency i.e. the amount of nitrogen fixed per 1 gm. of carbon oxidized is 14.6 milligrams in the light and 7.7 mg. in the dark. We have also observed in all our experiments on nitrogen fixation that the efficiency falls off as the intitial N content increases. It is expected that in Rothamsted where there is less sunshine that the efficiency in sunlight is likely to be 10 mgm. and 5 mgm. in the dark with a soil containing 0.196% N as in 1865. It appears that out of a total of 4000 lbs. of carbon added in the form of farmyard manure, 3000 lbs. may be oxidized per year and may fix 30 lbs. of nitrogen per acre per year. In subsequent years when the nitrogen content of the soil increases the efficiency will fall off and the nitrogen fixation per year may drop down to 15 to 20 lbs. per year. In 49 years from 1865 to 1914 the average nitrogen fixation or increase per year was actually 15.1 lbs. per acre. The same soil contained 0.2210% nitrogen *i.e.* 5235 lbs. nitrogen per acre in 1893 whilst in 1843, it was 0.122% corresponding to 2890 lbs. per acre. Hence the nitrogen fixed per acre is 2345 lbs. in 62 years i.e. 37.8 lbs. per year. In Woburn using 100 lbs. of nitrogen in the form of farmyard manure to a field containing 0.156% nitrogen upto 1888 the total nitrogen increased to 0.171% in the

years from 1876 to 1888 This experiment, therefore, shows a gain of 13 lbs of nitrogen per year

On the other hand, when 43 lbs of nitrogen as ammonium sulphate were added with minerals the soil nitrogen which was 0 122% *i e* 2890 lbs per acre in 1843 fell to 0 1107% i e 2629 lbs per acre in 1893 Nitrogen added in the form of manures in 50 years was 2150 lbs and the crop took up 40 lbs per year Rain and seed supplied 350 lbs in 50 years Hence there is a dead loss of 760 lbs in 50 years *i e* 15 5 lbs per year even when manured with 43 lbs of nitrogen per year in Rothamsted On the addition of 86 lbs of nitrogen per year the soil contained 0 119% *i e* 2818 lbs per acre Hence the loss from the soil is 72 lbs of nitrogen in 50 years during which period 4300 lbs of nitrogen were added as ammonium sulphate and the crop consumed 44 lbs per year *i e* 2200 lbs in 50 years Rain water and seed also supplied 350 lbs Hence the dead loss in this case is 50 5 lbs per year Moreover on the addition of 129 lbs of nitrogen as ammonium sulphate per year the soil nitrogen rose to 0 129% i e 3055 lbs per acre in 1893 whilst in 1843 it was 0 122% Hence in this case the gain in soil nitrogen is only 165 lbs in 50 years The manure added 6450 lbs and rain and seed another 350 lbs Hence the total added nitrogen is 6965 lbs out of which the crop took 46 lbs per acre per year *i e* 2300 lbs in 50 years In this case on the addition of 29 lbs of nitrogen as ammonium sulphate, the dead loss in 50 years is 4318 lbs *i e* 93 lbs per acre per year

On the other hand in the unmanured plot the nitrogen content in 1893 was 0 0990% *i e* 2345 lbs per acre whilst the original nitrogen was 0 122% *i e* 2890 lbs per acre Hence in this case the fall in nitrogen in the soil in 50 years is 545 lbs The crop was using 17 lbs per acre Hence the nitrogen balance is as follows —

Taken up by the crop	Rain water and seed	Difference
850 lbs	350 lbs	500 lbs

whilst the soil lost 545 lbs Hence the dead loss is only one pound per year per acre

It is clear, therefore, that when about 100 lbs of nitrogen are added in the form of ammonium sulphate even in England more than 60 lbs is lost without benefit to the crop or the soil and the majority of the nitrogen

added is lost. In India the loss is certainly greater as our experiments with ammonium sulphate reveal.

If intensive cultivation is done and if the soil nitrogen has to be maintained at a steady level we should be prepared to add nitrogen as ammonium sulphate to the extent of 100 lbs. of nitrogen per acre for a good crop yield but about 2/3rd of it may be lost as gaseous nitrogen. This loss is mainly due to the formation and decomposition of the unstable substance ammonium nitrite in the processes of ammonification and nitrification, which are oxidation reactions.

Russell and Voelcker[2] have emphasised that in Woburn experiments there were residual effects even of ammonium sulphate and sodium nitrate, although this has not been observed in Rothamsted. These observations can be readily explained from the viewpoint that when sodium nitrate, ammonium sulphate or any nitrogenous matter is added to the soil the crop will obtain their nitrogen requirements from these manures and not from the soil as happens when crops are grown in unmanured fields. Moreover, as there is more crop in the manured fields, the plant residues left in the fields after harvesting are larger in amount than in unmanured fields and hence more nitrogen fixation is possible in manured fields than in the unmanured ones. In foregoing pages it has been stated that when ammonium sulphate at the rate of 43 lbs. 86 lbs. and 129 lbs. per acre has been added annually the nitrogen content of the soil after harvesting the crop is greater than in the unmanured field and hence the crop produced in subsequent years will be larger in the former ones even without application of manure than in the latter. This is supported by the Rothamsted results showing that the total N content of the unmanured field is 0·095% against 0·099% using artificial manures.

It is well known that the chief object of starting the Woburn experimental station was to test experimentally whether the dung obtained from animals fed on decorticated cotton cake has better manurial value on soils than the dung obtained from corn feeding. After 50 years experiment Russell and Voelcker[3] stated as follows:

"A review of the results forces one to the conclusion that the experiments have entirely failed to show any marked superiority of cake feeding over corn feeding on this soil".

These unexpected results have not yet been explained by the workers in Rothamsted or Woburn but will be quite clear from the following considerations

In the Woburn experiments in the cake 45 lbs of NH_3 *i e* 37 lbs nitrogen were added per acre, whilst with corndung 18 lbs NH_3 added *i e* 14 8 lbs nitrogen were added

Now if we take C N ratio in corndung as 30 then the carbon added is 444 lbs per acre, out of which approximately 1/4th *i e* 111 lbs remains in the soil Then about 330 lbs of carbon is oxidised in the soil per year This may lead to a fixation of 6 lbs of nitrogen Hence the total nitrogen in the corndung is 6 + 15 lbs = 21 lbs per acre Even if we assume that the C N is 20 1 in corndung, the carbon added is 296 lbs per acre and if 150 lbs are oxidised yielding 2 lbs of fixed N and making a total of 17 lbs of nitrogen per acre The soil contains nearly 0 156% *i e* 3500 lbs total nitrogen and hence the tot l nitrogen in the cake dunged field is 3500 + 37 lbs = 3537 lbs and in corndunged field is 3500 + 21 lbs = 3521 lbs. per acre If we assume that about 2% of the total nitrogen is in the available form, then the available nitrogen becomes 70 7 lbs per acre in the cake dunged field and 70 4 lbs in the corndunged field and thus the crop should be identical

Even when the total nitrogen of the soil drops to 0 093% after continuous cultivation, the total nitrogen in the soil becomes 2082 lbs per acre and if 2% is in the available form then the available nitrogen becomes 41 6 lbs per acre But if we add the cake dung or corn dung, the total nitrogen in the cake dung becomes 2082 + 37 lbs = 2119 lbs making 42 4 lbs available nitrogen per acre, whilst with corn, the total nitrogen and available nitrogen become 2103 lbs and 42 lbs respectively This also should produce the same crop On the other hand, if nitrogen is added in the form of ammonium sulphate or sodium nitrate instead of the cake the position becomes different atonce as will be evident from the following lines —

The original available nitrogen present in the soil is 70 lbs per acre, whilst the available nitrogen added is 37 lbs (equivalent to the cake dung) and this makes 107 lbs per acre, whilst with corn dung equivalent of nitrogen added as ammonium sulphate or sodium nitrate, the total avai-

lable nitrogen comes upto 70 + 15 lbs = 85 lbs These amounts of available nitrogen should produce better crops than with dung, more so with the first case than in the second but both the crops should be better than with dungs This is corroborated by the Woburn experiments

SOURCE OF SOIL NITROGEN COMPOUNDS

According to Hall[4] leguminous plants or rather the bacteria with which they are associated are probably the original source of world's stock of combined nitrogen Russell[5] has stated "In England they had established that the source of nitrogen in the soil was leguminous plants But in the arid regions of U S A they failed to get clear evidence of fixation by leguminous plants" On the other hand Dhar[6] has emphasised that the nitrogen status of a soil is permanently increased by the addition of cow manure (farmyard manure) or other carbonaceous substances e g molasses, leaves, hay etc which are oxidised in the soil c using nitrogen fixation but not by legumes which do not leave a residual effect on the soil for long The sources of soil nitrogen is this fixation of atmospheric nitrogen and the added nitrogenous matter present in plant residues

This conclusion of Dhar is supported by the following classical observations made at Rothamsted and Woburn The Hoos field (Rothamsted) experiments with red clover were continued from 1849 to 1877 during which clover was sown 15 times but only produced a crop in seven years This land was divided into a number of small plots from 1878 and sown with various leguminous plants like lucerne, peas, beans, vetches etc At first a fair growth of some of the plants was obtained on the land which had ceased to carry red clover but in later years there were repeated failures of growth The land got very foul and in a poor mechanical condition Hence in 1898 the greater part of the land was sown with wheat without manure and the result showed that the leguminous crop left residual nitrogen in the soil but this residue was rapidly exhausted and after five years there was hardly any effect left It appears, therefore, that the continuous growing of leguminous crops is a difficult business and the residual effect lasts for a short time On the other hand the residual effect of farmyard manure is far more permanent Thus one of the permanent barley plots in Rothamsted received 14 tons of farmyard

manure containing 200 lbs of nitrogen per year from 1852 to 1871 It was then divided into two plots one of which received no manure of any kind, and the other continued to receive farmyard manure The produce in the barley plot on the half receiving no manure since 1872 was double of that obtained from the continuously unmanured plot even after 30 years In Rothamsted experiments with hay, farmyard manure was applied for the first 8 years at the rate of 14 tons per acre The application was discontinued but the beneficial effects lasted for 40 years Similar lasting residual effect of farmyard manure has been reported in the Woburn experiments [7] Moreover, a plot of land in the Geescroft field (Rothamsted) covered with grass without any leguminous plant showed an increase in nitrogen from 0 108 to 0 145 % in 20 years *i e* 44 lbs of nitrogen per acre per annum The following results were obtained on Broadbalk plots to which ammonium sulphate was annually added since 1844 and sodium nitrate since 1852 The original nitrogen in the soil was probably 0 122%

	Ammonium sulphate				Sodium nitrate		Farmyard manure
Nitrogen added per acre in lbs	None	43	86	129	43	86	200
Nitrogen in soil % in 1914	0 104	0 111	0 119	0 129	0 116	0 115	0 236

It appears therefore, that there was deterioration of soils with 43 lbs and 86 lbs but with 129 lbs nitrogen added as ammonium salt or nitrate the nitrogen of the soil remained practically stationary, whilst farmyard manure which can fix atmospheric nitrogen improved the soil status markedly Leguminous crops with a C/N ratio of about 12 to 13 adds total nitrogen temporarily and this is nitrified fairly quickly and the available nitrogen thus produced is partially absorbed by the crops and partially lost as nitrogen gas In this respect they resemble artificial farmyard manure (compost) Because of the presence of carbonaceous compounds in the leguminous crops the nitrification of the nitrogenous compounds is retarded to a certain extent and hence the residual effect may last for 2 to 5 years whilst with ammonium salts there is hardly any residual effect even in the second year Farmyard manure, however, with a C/N ratio of 20 or more has been found to fix atmospheric nitrogen and the carbonaceous compounds in farmyard manure preserve the soil nitrogen from rapid nitrification and loss by acting as negative

catalysts in the ammonication and nitrification processes, which are oxidation reactions and the residual effect may last for a very much longer period. The leguminous crops are plants of a very special variety and have to be aided by bacillus radicicola or other symbiotic bacteria for nitrogen fixation. These plants and bacteria do not occur in all soils. Hence it is difficult to assume the presence of these plants and bacteria in newly formed soils where nitrogen fixation takes place readily and this process may be a physico-chemical and non-biological reaction aided by light absorption. At a later stage in the evolution of the soil, Azotobacter and bacillus radicicola with legumes may appear and help in the soil enrichment. The recent report of Keen[8] that the residual effect of artificial manures in Cyprus is more pronounced than organic manures is contrary to the experiences in India, Ceylon, South Africa, French Morocco and Greece but his observations on the additions of organic matter to tropical soils are explicable from the viewpoint advanced here.

Summary

(1) Experimental results on manuring show that ammonium sulphate or sodium nitrate only improves crop production but does not increase soil fertility and the total nitrogen content of the soil. When 100 lbs. of nitrogen per acre of arable land are added as ammonium sulphate almost 65 lbs. are lost without benefit to the soil or crop.

(2) Cow dung, farm yard manure, leaves, molasses, hay etc. containing carbonaceous compounds not only fix atmospheric nitrogen and enrich the soil but act as a preserver of the nitrogenous compounds by functioning as negative catalysts in the processes of ammonification and nitrification, which are oxidation reactions. The loss of soil nitrogen is mainly due to the rapid nitrification of nitrogen compounds with the formation and decomposition of the unstable substance ammonium nitrite. Hence organic manures improve crop production and also the fertility of the soil permanently.

(3) It appears that the source of the world's stock of combined nitrogen in the soil is the fixation of atmospheric nitrogen by the oxidation of carbonaceous compounds present in the organic manures and the added nitrogenous compounds present in the plant residues. Farm yard manures leave beneficial effects on soils for 30 or even 40 years after their

addition, whilst legumes can have residual effect for not more than five years.

REFERENCES

(1) Russell-Soil conditions and Plant Growth page 361 (1932).

(2) Russell and Voelcker 50 Years of Field Experiments at Woburn page 51.

(3) Ibid page 23.

(4) A. D. Hall "Book of Rothamsted Experiments", year 1905, p. 14.

(5) Russell Address at Bangalore, Dec. 15, 1936.

(6) Dhar 'Nature' *151*, (1943), 590.

(7) Russell and Voelcker "50 Years of Field Experiments at Woburn" pages 158-161.

(8) B. A. Keen "The Agricultural Development of the Middle East", 1946, pages 48, 117-119.

OXIDATION OF EDIBLE SUBSTANCES BY HYDROGEN PEROXIDE WITH IRON AS CATALYST

By N. R. Dhar and B. V. S. Raghavan

(*Read on 15th September*, 1947)

Edible substances like fats, carbohydrates and proteins are easily oxidized in the animal body. In normal health slow and simultaneous oxidation of food materials containing fats and carbohydrates and proteins takes place but in diabetes glucose, which is the chief energy material under normal conditions does not take part in the oxidation. Hence the oxidation of the other materials like proteins and fats has to be hastened in the human body and this produces acetone bodies harmful to the system.

In this laboratory Chakravarti and Dhar[1] carried on experiments with hydrogen peroxide as oxidising agent in presence of ferric salt as a catalyst and in this paper our observations and results are recorded in extending the same line of investigation with other food materials.

Experimental

(a) 0.5 gr. of the organic substance was mixed with 50 cc. water to which 10 cc. of 11·2 vol. hydrogen peroxide were added with 1cc. of ferric sulphate, containing 0.005 gr. of iron. The mixture was kept at 50° for 60 hours. Then it was distilled and to the distillate which was free from hydrogen peroxide, 10 cc. of N/10 caustic soda and 10 cc. of N/10 iodine were added and was set aside for 10 minutes and the amount of iodine used up was estimated.

(b) 0.5 gr. of oil and 0.5 gram of dextrose were taken and 15 cc. of carbon tetrachloride were added. Then 50 cc. of a mixture containing equal volums of 5% alcoholic iodine and 6% alcoholic mercuric chloride which were mixed a day before were added to the oil and dextrose mixture which was left overnight and the amount of iodine used up per 100 gr. of oil was estimated.

(c) 0 5 gr of oil was taken and 10 cc of hydrogen peroxide and 1cc of the same ferric sulphate solution and 50 cc of water were added to the oil and this mixture was kept at 50° for 60 hours Then it was distilled free from hydrogen peroxide and the residue was treated in the manner described in (b) The difference between (b) and (c) gives the amount of oil oxidised in terms of iodine A small correction has to be applied for the amount of iodine taken up by dextrose in (b) and with 0 5 grm dextrose 0 02 gram of iodine was absorbed

It was observed by Dhar and collaborators[2 3] and by Moureu and Dufraisse[4] that the slow oxidation of substances is retarded by reducing agents which usually undergo oxidation along with the primary change

Not only fats and proteins produce compounds of aldehydic and ketonic nature but the carbohydrates as well The explanation is not far to seek The carbohydrates on oxidation give rise to glyceric aldehyde and lactic acid and these produce acetaldehyde[5] The higher fatty acids gradually undergo oxidation to compounds containing smaller amounts of carbon by β oxidation[6] and finally to butyric acid which may give rise to acetone bodies Proteins hydrolyse and give alanine and other amino acids These in turn produce acetaldehyde and other aldehydic bodies

Oxidation of sodium tartrate, sodium citrate, sodium oxalate, sodium acetate, butter, ghee, gingeli oil, castor oil, cocoanut oil, groundnut oil, mustard oil, lactic acid, stearic acid, sodium palmitate, sodium oleate, yellow of the egg, white of the egg, and dextrose was studied and also the effect of varying the amount of dextrose from 0 5, 1, 1 5, to 2 grs A glance at the table no 1 shows that sodium tartrate tops in the list in the formation of acetone bodies when it is individually oxidised (table no 1, column no 2) with hydrogen peroxide Then come palmitate and oleate, dextrose, and ground nut oil Ground nut oil and dextrose are comparable in their oxidisability When oxidised alone yellow of the egg, butter, ghee give small amounts of acetone bodies (0 02gr) stearic acid gives the least amount of acetone bodies (0 005gr) Yellow of the egg gives greater amount of acetone bodies than the white (0 0199 against 0 0141gr)

TABLE I

Amounts of acetone bodies got (in terms of iodine) with 0·5 gr substance + carbohydrate.

1	2	3	4	5	6
Substance.	Acetone bodies with H_2O_2 only	Acetone bodies with H_2O_2 + 0.5gr Dextrose	Acetone bodies with H_2O_2 + 1gr Dextrose.	Acetone bodies with H_2O_2 + 1.5 grs Dextrose,	Acetone bodies with H_2O_2 + 2grs Dextrose.
Sodium tartrate.	0.1709	0.0034	0.0072	0 0093	0.0098
Sodium palmitate.	0.1370	0.0039	0.0059	0.0079	0 008
Sodium oleate.	0.1094	0 0052	0.0073	0.0092	0.0097
Sodium acetate.	0.0976	0.0046	0.0092	0.0111	0.0113
Sodium citrate.	0.0939	0 0081	0.0123	0.0141	0.0144
Sodium oxalate.	0 0893	0.0116	0.0152	0.0171	0.0171
Dextrose.	0.0765	....	....	....	....
Ground nut oil.	0.0720	0.0214	0.0234	0 0251	0.0269
Cocoa nut oil.	0.024	0.0059	0.0069	0.0079	0.0079
Lactic acid.	0.0204	0.0069	0.0069	0 0079	0.0079
Mustard oil.	0.0204	0.0073	0.0073	0.0082	0.0079
Castor oil.	0.0204	0.0039	0.0047	0 006	0.0074
Yellow of the Egg.	0.0199	0.0041	0.0047	0.006	0.0074
Butter.	0.0157	0.0059	0.0067	0 0067	0.0079
Ghee.	0.0153	0.0067	0 0059	0.0052	0.0079
White of the Egg.	0.0141	0.0061	0 0063	0.0071	0.0074
Gingeli oil.	0.0139	0.0067	0.0067	0.0073	0.0079
Stearicacid.	0.0059	0.0067	0.0052	0.0073	0.0079

Then 0.5gr. of each of the above substances was mixed with 0.5gr. of dextrose (table no 1, column 3). Sodium tartrate which gives the maximum amount of acetone bodies in the 2nd column now produces minimum amount (0.0034gr against 0.1709gr) In this series of experiments ground nut oil gives the maximum amount of acetone bodies (0.0214gr.) Ghee, butter, mustard oil give acetone bodies of the order of about (0.008gr). Hence the marked effect of dextrose in lowering the formation of acetone bodies.

For example taking the minimum case in column 3, table no 1 *viz.* 0.5gr. of dextrose and 0.5gr. of tartrate give 0.0034gr. of acetone bodies while they ought to give 0.0765 + 0.1709 = 0.2474gr had there been no retardation.

The effect of increasing the amount of dextrose from 0.5, 1, 1·5, to 2 grs. was also investigated (table 1 columns 3,4,5,6). The amount of acetone products formed rises with the increase in the amounts of dextrose (upto 1.5gr. of dextrose) in the case of sodium tartrate, palmitate, citrate

namely with substances which give high amounts of acetone bodies when they are individually oxidised with hydrogen peroxide With slowly oxidisable substances like butter, ghee changing the amounts of dextrose has relatively smaller effect

The mixed oxidation of fat, carbohydrate and protein was also studied (table 2) In this series of experiments dextrose and fat together were mixed with the white of the egg or yellow of the egg and the effect was studied With white the maximum amount of acetone bodies is given by sodium tartrate (0 0134gr column 2 table 2) and the minimum with lactic acid (0 0068gr) Ghee and butter give about 0 008gr With the yellow of the egg the maximum is given by tartrate 0 0041gr and the minimum by butter, ghee, and mustard oil (column 3 table 2) Here also the decrease of the acetone body formation in the mixed oxidation of fats and proteins and carbohydrates is apparent From the table we can see that the amount of acetone bodies got by the yellow of the egg is much smaller than the acetone bodies given by the white (the ratio is about 1 3)

TABLE 2

Amounts of acetone bodies got in terms of iodine in the mixed oxidation of 0 5 gr Fat + 0 5 gr protein + 0 5 gr Dextrose

Substance	Acetone bodies with 0 5gr Dextrose + 0 5 white of egg	Acetone bodies with 0 5gr Dextrose + 0 5gr of yellow of egg
Sodium tartrate	0 0134	0 0041
Sodium palmitate	0 0131	0 0039
Sodium oleate	0 0130	0 0041
Sodium acetate	0 0125	0 0041
Sodium citrate	0 009	0 0034
Sodium oxalate	0 0099	0 0041
Ground nut oil	0 010	0 0039
Lactic acid	0 0068	0 0024
Mustard oil	0 0073	0 0023
Castor oil	0 0093	0 0023
Butter	0 0079	0 0023
Ghee	0 0079	0 0027
Gingeli oil	0 0093	0 0059
Stearic acid	0 0084	0 0039
Cocoanut oil	0 008	0 0031

By the iodine value determinations it was studied whether when a fat is mixed with a carbohydrate it is undergoing retardation or not (table 3). From the table of iodine values the difference in the values in the columns 2 and 3 gives the amount of oil oxidised and the difference of the values in columns 5 and 3 gives the amount of retardation.

TABLE 3

Iodine values etc. in the Oxidation experiments performed.

1	2	3	4	5	6
	Iodine used up per 100 grs of oil after correction for dextrose.	Iodine used per 100 grs. of oil with H_2O_2 only.	Amount of oil oxidyzed in terms of iodine.	Iodine used up per 100 grs. of oil + H_2O_2 + Dextrose.	Amount retarded in terms of iodine (after correction for dextrose).
Castor oil.	85·1	69·1	16	73·2	4·12
Cocoanut oil.	9·1	1·21	7·89	2·45	1·26
Ground nut oil.	73·9	18·4	55·5	53·85	25·47
Mustard oil.	100·4	83·2	17·2	88·2	5·02
Butter.	30·1	17·8	12·3	21·2	3·42
Ghee.	29·5	17·4	12·1	20·7	3·32
Gingeli oil.	109·6	96·3	3·3	100·6	43·2

CONCLUSIONS

1. Ground nut oil appears to form as much of acetone bodies as dextrose.

2. The amount of acetone bodies obtained in the mixed oxidation of either fat and carbohydrate or fat, carbohydrate and protein is much smaller than the sum of the amounts of acetone bodies which each gives rise to individually.

3. With substances which form large amounts of acetone bodies when individually oxidised the amount acetone bodies formed tend to rise with increasing amounts of dextrose. With slowly oxidisable substances like ghee, butter etc. rise in the amount of dextrose has not much effect.

4. Yellow of the egg generates 1/3 the amount of acetone bodies which the white gives in the presence of carbohydrate and fat.

These results are in general agreement with those obtained previously in this laboratory.

References

1. Chakravarti and Dhar (*J. Ind. Chem. Soc.* 1929, **6**, 617).
2. N. R. Dhar—*Proc. Akad. Wet. Amsterdam* 1921, **29**, 1023.
3. „ —*Z. anorg. Chem.* 1925, **144**, 289.
4. Moureu and Dufraisse—*Compt. Rend.* 1924, **179**, 237.
5. Ray :—*J. Gen. Physiol* 1924, 6, 509, 528.
6. Beitr, *Chem. Physiol Path.*, 1908, 22, 411.

INVESTIGATIONS ON NICKEL AMMINES

Part I *Isolation of Nickel Ammine Thiocyanates*

By C. S. Shaw and S. Ghosh

Physical Chemistry Laboratory, Allahabad University

Abstract

Two new methods of preparation of Tetra and Tri ammoniate nickel thiocyanates have been described

Introduction

It is well known that a solution of ammonium hydroxide when added to cobalt nickel and copper salt solutions gives a precipitate of the hydroxides of these metals which dissolve in an excess of the reagent forming complex ammines

A large number of cobalt[1] and copper[2] ammines have been investigated by numerous workers Some complex ammines of nickel salts notably those of nickel halides, nitrates, sulphate and phosphate, have also been isolated.[3]

The present investigation has been undertaken in order to find out if there exists any co relation between the composition and properties of the various nickel ammines with those of cobalt and copper

Nickel thiocyanate tetra ammoniate $Ni(CNS)_2 \cdot 4NH_3$ was first mentioned by Meizendroff[5] Bohart[6] however found that Meizendroff's compound corresponded to nickel thiocyanate tri ammoniate He further prepared nickel thiocyanate ammoniates with 2, 3, 4, 5½ and 8 mols of ammonia A tri ammoniate has also been mentioned by Peters[7]

The method of preparation of the tetra ammoniate compound used previously was by adding an equivalent amount of ammonium thiocyanate solution to a hot saturated solution of nickel sulphate, then adding ammonia solution till there is a strong smell of ammonia This solution when left for crystallisation, yielded the tetra ammoniate compound

In this paper two new methods of isolation of the tetra and the tri ammoniate nickel thiocyanate have been described

EXPERIMENTAL

The sulphate ion, from nickel sulphate was first removed from a mixture of a nickel sulphate solution containing ammonium thiocyanate, by adding requisite amounts of barium hydroxide solution and simultaneously adding excess of ammonium hydroxide solution The insoluble barium sulphate was then filtered out and the filtrate set apart for crystallisation

It was found that the ammonia escaped very quickly and unless the solution was very concentrated it had a tendency to hydrolyse In the next attempt therefore, nickel thiocyanate was prepared and simultaneously converted to the ammine complex by treating a mixture of solid nickel sulphate and barium thiocyanate with concentrated ammonia solution The method of obtaining nickel thiocyanate depended on the formation of this compound by the interaction of barium thiocyanate and nickel sulphate in the reaction mixture when barium sulphate separated out The nickel thiocyanate then reacts with ammonia to give the ammine complex

To a weighed quantity of nickel sulphate ($NiSO_4 \cdot 7H_2O$) an equivalent amount of barium thiocyanate was added in the solid state. To this, a measured volume of concentrated aqueous ammonia solution was added, the precipitated barium sulphate filtered off and the filtrate was set apart for crystallization at a room temperature (30°) After leaving it over night crystals were found to have been formed These crystals were separated, dried quickly by pressing between layers of filter paper and in order to avoid loss of ammonia from the crystals, they were kept in a well corked glass tube in a dessicator filled with ammonia vapours, over lime

It was found that a good yield of the crystals could be obtained by using at least 1/10 th molar quantity of nickel sulphate, an equivalent amount of barium thiocyanate and atleast 50 60cc s of approximately 11 M ammonia solution With a more dilute solution of ammonia the filtrate, hydrolyses on standing

Nickel in the crystals was estimated as the dimethylglyoxime compound, ammonia by the Kjeldhals' method and thiocyanate by the Volhard method

The analytical results found

	Nickel	Thiocyanate	Ammonia	Total	Ratio Ni	Ratio NH_3	Molecular formula
	24 20	47 67	27 68	99 55	1	3 971	The ratio of Ni CNS was found to be 1 2 Water of crystallization absent Hence Molecular formula Calculated $Ni(CNS)_2\ 4NH_3$
Calculated	24 29%	47 72/	27 99%	100 00/			

The tetra ammoniate compound thus obtained by us, smells very slightly of ammonia Has a saphire blue colour with violet tinge The surface layer of the salt gradually tarnishes when exposed to air because of the loss of ammonia The salt is soluble in ammonia solution giving a greenish blue, blue and violet blue solution, depending on the increasing concentration of ammonia

It will be seen that in the method described above the ammonia compound that crystallizes out is mainly the tetra ammoniate nickel thiocyanate, provided precautions are taken to avoid the loss of ammonia from the crystals The second crop of crystals from the above which we expected to be a lower ammonia containing compound, when analysed proved to be a mixture of tetra and lower ammonia containing compounds for obvious reasons Any attempt to prepare pure lower ammonia containing nickel thiocyanate ammoniates, by the same method, by using more dilute solution of ammonia proved fruitless, because of the hydrolysis that occured during crystallization Hence another method was adopted for the preparation of these complexes by taking nickel carbonate and ammonium thiocyanate as the starting material

For this, a sample of Merck's nickel carbonate (basic) was taken and its nickel content estimated To a weighed quantity of nickel carbonate 1/10th molar, 50ccs of fairly concentrated solution of ammonium thiocyanate (approximately 60% solution) were added, the solution warmed when there was a vigorous effervesence with the evolution of carbon dioxide and some ammonia The solution was filtered and set aside for crystallization at a room temperature (26°) when small blue crystals separated out

after some time The crystals were dried by pressing between layers of filterpaper and kept in a well corked glass tube

The analytical results found are

Total Analysis				Ratio		Molecular Formula
Nickel	Thiocyanate	Ammonia	Total	Ni	NH_3	
26 2	50 89	21 89	98 98	1	2 900	The ratio of Ni CNS was found to be 1 : 2 Water of crystallization absent Hence molecular formula $Ni(CNS)_2 \cdot 3NH_3$
Calculated	26 11%	51 32%	22 57/	100 00		

The triammoniate compound thus obtained by us does not smell of ammonia Has a blue colour and does not tarnish for some time when exposed to air The salt is soluble in moderately concentrated ammonia solution giving a greenish blue solution, but hydrolyses like the tetra ammoniate compound in aqueous solution with the precipitation of nickel hydroxide

Conclusion

More work is in progress to isolate pure sample of higher ammine compounds of nickel for a complete study of the various nickel ammine complexes

References

1 Mellor—A comprehensive treaties on Inorganic and Theoretical Chemistry—Vol XIV

2 Dey and Bhattacharya—*Pro Ind Aca Sci* 1946, **23** No 5A 259 260

3 Mellor—A comprehensive treaties on Inorganic and Theoretical Chemistry Volume XV

4 Meizendroff—*Pogg Ann*, 1842, **56**, 63

5 Bohart—*J Phys Chem* 1915, **19**, 537-563

6 Peters—*Ber*, 1908, **41**, 3178

STUDIES IN THE PRODUCTION OF YEAST

By N. R. Dhar and Krishna Bahadur

Chemical Laboratory, Allahabad University.

Pasteur in his classical researches on 'Fermentation' described this phenomenon as 'Life without air (La vie sans l'air)' because the chemical change involved in fermentation is as follows :—$C_6H_{12}O_6 = 2\ CO_2 + 2\ C_2H_5OH + 25K$ Cals and free oxygen does not take part directly in the process.

In ordinary fermentation of sugars into alcohol Pasteur was the first to demonstrate that yeast can live in the presence of only small traces of oxygen. Since the growth of yeast is abundant in the process of fermentation and the small amount of oxygen present is used up rapidly, it can be assumed that the greater part of the development of yeast can take place in the absence of free oxygen. The energy requirement of the yeast is met with by the heat of the reaction as stated above.

We have carried on numerous experiments on the production of yeast by using different energy materials and have found that yeast can grow vigorously using even alcohol and starch as energy materials specially when air is passed.

In our experiments on the growth or yeast (Torula variety containing 6.8% N and 22.8% C.) we have used analytically pure starch of 1% strength and have passed a current of air. The temperature was maintained at 30°; without passing air hardly any growth of yeast is observed.

Similarly we have obtained a vigorous growth of yeast by passing air in dilute solutions of alcohol. In this reaction the presence of any carbohydrate is not essential. The dilute alcohol without any other energy material is slowly oxidized by air in presence of yeast and supplies energy according to the following equation :—

$C_2H_5OH + 3O_2 = 2\ CO_2 + 3\ H_2O + 325$, K. Cals. and a part of the alcohol seems to be assimilated by yeast for building its body materials. We believe that the same thing happens with starch. By passing air,

we have been able to grow yeast even in solutions or suspensions of glycerol, gelatine, oils, urea, ammonium sulphate, microcosmic salt, sodium nitrite, sulphur sulphite, thiosulphate, ferrous oxide, metallic aluminium zinc, space cobalt, iron etc used as food materials

India being chiefly as yet an agricultural country has an abundant supply of raw materials for yeast manufacture *e g*, rice, barley, maize, wheat and potatoes, molasses etc Another raw material on which so far no attention has been paid is toddy With the coming of prohibition in the country, toddy may become a useless product Fresh samples of toddy have been analysed in these laboratories and were found to contain approximately 13 4 gms of sugar per 100 cc of fresh toddy which yielded 1 25 gms of yeast without passing air

The effect of nitrates and phosphates of sodium potassium and ammonium on the growth of the Torula variety of yeast have been studied It has been observed that ammonium nitrate increases the yeast growth, sodium phosphate has also a beneficial effect while potassium ions have a slight toxic effect on the growth of yeast The effect of negative ions like acetates, chlorides, sulphates etc , on the growth of yeast and alcohol formation have also been investigated It is found that the presence of an excess of sulphate ions in the culture decreases both alcohol and yeast formation Acetate ions favours yeast formation but retards alcohol production, while chloride ion favours alcohol formation but retards yeast generation In the control experiments the yield of yeast was 10 2% of the sugar fermented and it increased to 12 05% if acetate ions were present and decreased to 9 75% if sulphite ions were present Small sugar concentrations were found favourable for yeast growth while at higher concentration there is a tendency for alcohol production in larger quantity

The effect of toxic substances on the growth of yeast and alcohol production has been studied —

As, O_3, $CuSO_4$, $Sb_2(SO_4)_3$, $FeSO_4$ and $MgSO_4$ retard the growth of yeast but $ZnSO_4$ in low concentrations accelerates the yeast growth while in higher concentrations retard it

The effect of light on the growth of yeast has also been studied and it is found that diffused light is beneficial for the growth of yeast

Very interesting results have been obtained by growing yeast by passing air in medium containing small amounts of alcohol or starch and necessary inorganic salts in the complete absence of sugar:—

Tempt. 25 30°

Medium	Grs. yeast produced	Yield of yeast on the wt. of alcohol or starch
750 c.c. of culture medium containing 7 5 gms. alcohol	2.7188	36.25%
750 c.c. of culture medium containing 7 5 gms. of starch	2.1563	28.75%

It is obvious that the energy liberated by the oxidation of alcohol and starch which are exothermal reactions, is utilized by the yeast for its functions of life and growth. This has a great industrial bearing for yeast can be grown in waste liquors from different industries containing small percentages of alcohol which can not be recovered easily by the ordinary methods. We have been successful in decreasing the alcohol content of wines and converting a part of the alcohol into yeast which is an excellent food material. We are in touch with wine-makers and advising them to prepare healthy wines by aerating them and in this process a part of the alcohol is converted into a nourishing food. The Germans live a good deal on beer especially in summer months. German beer is rich in yeast but poor in alcohol.

Experiments are in progress to obtain yeast in large quantities and study the mechanism of alcoholic fermentation and yeast production and to preserve its vitamin contents.

QUANTITATIVE STUDY OF THE EXTENT OF INHIBITION OF THE PRECIPITATION OF STANNIC SULPHIDE IN PRESENCE OF SOLUBLE TARTRATES

By Arun K Dey

Department of Chemistry, University of Allahabad

(Communicated by Dr S Ghosh, D Sc F N A Sc)

(Read on 26th April, 1947)

Abstract

This paper is a continuation of the work of Dey and Bhattacharya,[1, 2] on the study of the inhibition of the precipitation of stannic sulphide in presence of various organic acids and their salts The extent of inhibition in the presence of sodium tartrate has been quantitatively studied The inhibition has been ascribed to be due to complex formation

Introduction

In a recent publication[1] Dey and Bhattacharya have shown complex formation to be the cause of the non precipitation of stannic sulphide in presence of oxalic acid and oxalates In other publications[2, 3] they have reported, that the same inhibition is possible in presence of other dicarboxylic acids as well It is well known (cf Rössing[4]) that the addition of oxalic and tartaric acids can be used to keep tin in solution, when antimony can be precipitated as sulphide by sulphuretted hydrogen

Stannic tartrate was known to exist,[5] since long, and complex formation between tin and tartaric acid was recorded by various earlier workers[6, 7] Also, the study of complex tartrates has been the subject of many investigations and in recent years Darmois and coworkers,[8] Vaishya and Raman[9] and Biswas[10] have dealt with this topic in considerable detail In a very recent publication,[11] Bobtelsky and Jordan have

described the results of their investigations on the complex tartrates and citrates of various metals.

During the preliminary experiments, I have observed that tartaric acid itself is unable to act as an inhibitor in the precipitation of stannic sulphide, whereas soluble tartrates show appreciable activity in this respect. In this paper, the results obtained on using sodium tartrate as an inhibitor is described.

Experimental

A solution of Schuchardt's stannic chloride was prepared in normal hydrochloric acid, and tin was estimated gravimetrically. Standard solutions of sodium tartrate of various concentrations were also prepared. A solution M/5 sodium sulphide was prepared by iodometric standardisation. It was noted that M/5 was the minimum strength of sodium sulphide, which could precipitate stannic sulphide completely from the stannic chloride solution. Since the stannic chloride solution was acidic, the mixture after the addition of an equal volume of sodium sulphide remained acidic.

Several test tubes were taken, and in each were delivered 10 c. c. of 0·09389 M of stannic chloride solution. Now 10 c. c. of the tartrate solutions of known concentration were added, and then 10 c. c. of the sodium sulphide solution. The first was filtered immediately after the addition of sodium sulphide, the second after half an hour, the third after four hours, the fourth after eight hours and the fifth after ninety-six hours. Different sets were taken, using different concentrations of the tartrate solution. A blank experiment, using water instead of the tartrate was also performed. The experiments were performed at a room temperature of 30 °C.

The precipitated stannic sulphide was filtered and estimated as oxide. The filtrates were boiled, and a further quantity of 1 c. c. sodium sulphide solution added, this was left overnight and the stannic sulphide now precipitated was filtered and estimated. The sum of the amounts of stannic oxide estimated in the precipitate and the filtrate corresponded to the total amount of tin available in the solution.

In the following table, the results obtained on the inhibition of the precipitation in presence of different quantities of tartrate are recorded

PERCENTAGE OF INHIBITION

IV Sn	$C_4H_2O_6$	Time after which filtration was done				
		0 hour	½ hour	4 hours	8 hours	96 hours
1	0	2 35	2 35/	1 90/		
1	0 665	11 78	11 50	11 28	10 42/	9 28/
1	1 33	15 24	13 34	12 08	11 29	10 36
1	2 66	18 50	15 32	14 12	13 75	12 03
1	5 32	33 71	26 21	25 28	23 62	22 51
1	10 64	43 31	33 59	30 65	28 01	26 28
1	15 96	56 01	42 21	38 73	32 58	29 36
1	21 28	69 28	48 73	40 38	36 71	33 05

In all the cases the inhibition is more marked at first, but soon the precipitation commences After a period of ninety-six hours a considerable portion of the tin is precipitated as stannic sulphide Here too, as in the case of oxalic acid and potassium oxalate (loc cit) the precipitate varies in nature, and shows a wide range of colours, beginning from yellow to deep brown, depending on the concentration of the tartrate used When the ratio tin tartrate is 1 10 64, the precipitate becomes highly gelatinous in nature, and resembles a freshly obtained precipitate of ferric hydroxide, in appearance When the quantity of tartrate was increased further, the system assumed a colloidal character and a considerable portion passed through the filter paper

In another set of experiments, the stability of the complex was studied, by allowing stannic chloride and tartrate solutions to remain in contact for different lengths of time, and then stannic sulphide was precipitated with sodium sulphide The precipitate obtained was filtered immediately after the addition of sodium sulphide, stannic oxide was estimated in the precipitate and the filtrate as before From these experiments it was inferred, that the inhibition does not depend on the period for which the solutions of stannic chloride and sodium tartrate are

allowed to stand together Thus the complex formed is quite stable and shows no tendency of decomposition, even when allowed to stand for ninety six hours

SUMMARY

1 The extent of inhibition of the precipitation of stannic sulphide from acidic solutions of stannic chloride have been studied quantitatively

2 The inhibition has been ascribed to be due to complex formation between stannic tin and soluble tartrates

3 It has been found that an appreciable quantity of sodium tartrate has to be added to perceive appreciable inhibition of the precipitation

4 It has been observed that the formation of a colloid precedes complex formation, and the colloidal matter settles with time The quantity of tin remaining in solution after the coagulation of the colloid gives an idea of the amount of complex formed

REFERENCES

1 Dey and Bhattacharya, *Proc Nat Acad Sci*, India 1946, **15**, 86
2 D y and Bhattacharya, *Current Science*, 1945, **14**, 70
3 Dey *University of Allahabad Studies*, 1946, **22**, 7
4 Rossing, *Zeit anal Chem*, **13**, 1
5 Bouquet, *J Pharm*, **11**, 460, Annalen, 1848, **64**, 278
6 Schiff, *Annalen*, 1863, **125**, 146
7 Henderson and coworkers *J C S* **75**, 154, Chem Centr, 1899, **1**, 1508
Rosenheim and Arons, *Zeit anorg Chem*, 1904, **39**, 171
8. Darmois and coworkers *Various papers Compt Rend* 1923 32
9 Vaishya and Raman *J Ind Chem Soc* 1934, **11**, 178
10 Biswas, *J Ind Chem Soc*, 1945, **22**, 351
1 Bobtelsky and Jordan, *J Amer Chem Soc*, 1945, **67**, 1824

STUDIES IN THE DYES DERIVED FROM QUINOLINIC ACID AND CINCHOMERONIC ACID AS ADSORPTION INDICATORS IN ARGENTOMETRIC TITRATIONS

PART II*

By R C Mehrotra

Chemical laboratories, the University of Allahabad, Allahabad

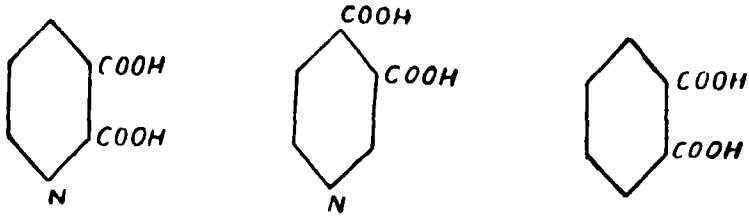
In a recent communication[1], the use of resorcinol quinolein and cinchomeronein as adsorption indicators in the titrations of halide solutions singly has been described In the present communication the behaviour of these dyes in mixed halide solutions and also, a comparision between the behaviour of these dyes and that of resorcinol phthalein has been studied Further, the tetrabromo derivatives of these dyes have been prepared and their applicability as adsorption indicators has been investigated

Titrations of mixed halide solutions —Belladen and Piazza[2] have observed that although Brilliant Archill C and Chromotrop F4B are suitable indicators for all the chloride, bromide and iodide ions separately, yet when a mixture of iodide and chloride ions is titrated against silver ions, the end point (pink⟶grey green) occurs, when silver nitrate equivalent to only the iodide ions present has been added The dyes under investigation (resorcionol quinolein and cinchomeronein) are also quite suitable for all the three halide ions, but they mark the end point when the total of all the halide ions present in the solution has been precipitated The addition of ammonium carbonate does not allow the iodide ions to be titrated alone in the presence of chloride ions

Comparison of the Applicability of these two dyes with fluorescein —The resorcinol quinolein and cinchomeronein dyes can be employed in ammoniacal as well as acidic solutions Unlike fluorescein these dyes can

*Read before the meeting of National Academy of Sciences, held in September 1947

be employed in the pH range 2 to 12 It has been found that in the case of ammoniacal solutions, the cinchomeronein indicates the end point only upto a concentration of N/30 to N/20 ammonia in the solution to be titrated, whereas in the case of quinolein, the end points are quite sharp in solutions in which the concentration of ammonia is as high as N/3 to N/2 Thus the cinchomeronein shows a behaviour midway between the pathalein and the quinolein and so it can be inferred that the substitution of the 'CH' group of benezene by the basic N' in pyridine is the controlling factor in the variation of these properties and the near ness of the 'N' atom to the carboxylic groups in the quinolein confers greater contrast to its properties than it does in the case of the cinchomeronein



The tertiary 'N' atom, as is well known, has got a powerful tendency to donate its lone pair of electrons, and this tendency will result in the formation of a chelate ringed compound, similar to that shown by Cox and coworkers[8] in the simpler case of argentic picolinate The chelation always lowers the solubility of a compound and thus the applicability of these dyes in acidic as well as ammoniacal media can be explained on the view point of the formation of highly insoluble chelate compounds with silver

Tetrabromo Resorcinol Quinolein and Cinchomeronein as Adsorption Indicators

Preparation of the dyes—The bromination of the quinolein and cinchomeronein was carried out in the alcoholic solution, and the tetrabromo derivatives were prepared and purified 0 2% solutions of the dyes were prepared in alcohol and these solutions used as indicators throughout these investigations.

Titration of Iodide Ions against Silver Ions· When a neutral solution of potassium iodide is titrated against silver nitrate, the coagulation of

the precipitate begins much before the end point and the precipitate appears as a deep pink mass at the equivalent point In the case of cinchomeronein, the colour of the coagulated particles remains yellow so long as iodide ions are present in excess and changes to pink with half a drop of the silver nitrate solution in excess, and simultaneously the pink colour of the suspension is discharged In the case of the tetrabromoquinolein the particles have a pinkish shade much before the equivalent point and the end point is indicated merely by the disappearance of the pink colour of the suspension at the equivalent point However, in acidic or ammoniacal media, the colour change at the end point becomes much sharper with both the indicators In the acidic solutions, the coagulation occurs just at the equivalent point So long as the iodide ions are present in excess, the suspension remains yellow and changes sharply to pink at the end point In the presence of ammonia, the coagulation of the silver iodide begins early However, the colour on the particles remains yellow with both the indicators and changes to pink with half a drop of the silver nitrate solution at the end point Along with the colour change on the particles, the pink colour of the supernatant suspension is also discharged simultaneously at the end point

Titration of Bromide Ions against Silver Ions When the bromide solutions are titrated against silver ions using tetrabromo quinolein or cinchomeronein as indicators, no sharp colour change at the end point could be obtained in the neutral solutions The end points did not improve also by the addition of ammonia However, in the presence of acetic acid the end points are very sharp and the titrations can be carried out accurately In the case of the cinchomeronein, the suspension remains yellow and becomes pink just at the equivalent point, whereas in the case of the quinolein the suspension assumes a slight pinkish shade before the end point and the equivalent point is indicated by change of the colour of the suspension from light pink to deep pink The end points are made much more sensitive, because the coagulation of the precipitate occurs immediately at the end point

Titration of Thiocyanate Ions In the case of the thiocyanate ions also, no sharp end points could be obtained in the neutral as well as in

ammoniacal media In the presence of acetic acid, the end points are quite sharp The coagulation occurs much earlier and the particles assume a slight pinkish shade from the beginning, but there is a sharp colour change from light pink to deep pink on coagulated particles at the end point

Titration of Chloride Ions In the case of the chloride ions no sharp colour change could be obtained either in the neutral or in ammoniacal or acidic media Even in the acidic solutions, the coagulation of the precipitate and the adsorption of the dye occurs much before the equivalent point which indicates that the dye anions are so strongly adsorbed by the precipitated silver chloride particles that they displace even the adsorbed chloride ions

Titration of Iodide Ions in Presence of other Halide Ions It is in this field that the indicators have been found to be of practical value When a mixture of iodide and chloride ions is titrated against silver ions in neutral or acidic media, the end point, indicated by the complete transference of the pink colour of the suspension to the particles of the coagulated precipitate, occurs after the whole of the iodide ions and the chloride ions has been precipitated However, in the presence of ammonia, the iodide ions alone can be titrated in the presence of chloride ions When a mixture of the iodide and chloride ions is titrated against silver ions in ammoniacal medium, the coagulation of the silver iodide particles begins soon, but the particles remain yellow When all the iodide ions have been removed as silver iodide, half a drop of the silver nitrate solution changes the yellow colour on the particles to pink with a simultaneous disappearance of the pink colour of the suspension The estimation of the iodide ions is accurate, when the ratio of the chloride iodide ions present has a value upto 1 2 In the presence of a greater proportion of the chloride ions, an excess of the silver nitrate solution is required

Attempts have been made to estimate the iodide ions in the presence of the bromide ions and also of ths bromide ions in the presence of the chloride ions, but the results were unsatisfactory Similarly the iodide ions could not be liberated in the presence of the thiocyanate ions

Volume & conc of halide solutions	Drops of indicator	Volume & conc of $AgNO_3$ solution	Transition of colour	Remarks
10 c c of N 10 KI	2	9 97 c c to 9 98 c c of N/10 $AgNO_3$	Pink suspension →Pink precipitate	Coagulation of the ppt occurs much before the end point In case of quin the particles assume pinkish shade before the end point
10 c c of N/10 KI+4 to 10 c c of N HAc	2	10 to 10 02 c c of N/10 AgNO	Yellow suspension ⟶ Pink ppt	The end point is much sharper than in the neutral soln The coagulation occurs just at the end point
10 c c of N/10 KI+6 to 8 c c of N NH_4OH	2	10 0 c c of N/10 $AgNO_3$	Yellow ppt ⟶ Pink ppt	The end point is very sharp Coagulation occurs much earlier but the end point though occurring on the coagulated particles is quite reversible
10 c, c of N/10 KI+5 c c ofN/10 KCl	2	14 94 to 14 98 c c of N/10 $AgNO_3$	Pinkish suspension ⟶ Pink ppt	The colour change at the end point is not very sharp The end point is indicated by the transference of the pink colour from suspension to ppt
10 c c of N 10 KI+3 to 5 c c N/10 KCl+ 4 c c of N NH_4OH	2	10 0 to 10 04 c c of N 10 $AgNO_3$	Yellow ppt →Pink ppt	The end point, though occurring on the coagulated particles is very sharp With larger proportions of chloride ions an appreciable over consumption of silver ions is required
10 c c of N/10 KCNS +6 to 8 c c of N HAc	2	10 0 c c of N/10 $AgNO_3$	Light pink ppt →Deep pink ppt	The end point is very sharp and quite reversible

Summary

1 A comparision of the applicability of resorcinol quinolein, cinchomeronein, and phthalein as adsorption indicators has been made and the differences have been explained

2 The behaviour of the indicators in the mixed halide solutions has been investigated

3 Two new indicators tetrabromo quinolein and tetrabromo cinchomeronein have been described

4 The new indicators are suitable for the titration of iodide, bromide and thiocyanate ions in acidic solutions

5 The iodide ions can be estimated very accurately in ammonical solutions also

6 Mixtures of iodide and chloride ions can be analysed completely by the help of these indicators The whole of the iodide and chloride ions can be determined by titration in neutral or acidic medium, and the iodide ions can be estimated alone by titration in presence of ammonia

In conclusion, I beg to offer my grateful thanks to Prof N R Dhar for his kind interest and encouragement during the course of this investigation

References

1 Mehrotra, *Proc Nat Acad Sciences* (Alld), 1946, 15, 148
2 Belladen & Piazza, *Ann Chim appl*, 1932, 22, 631
3 Cox et al, *Jour Chem Soc*, 1936, 775

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1947

PART II] SECTION A [VOL. 16

STUDY OF THE PREPARATION AND PROPERTIES OF ARGENTOTHIOSULPHATE COMPLEXES AND DETERMINATION OF THE VALENCY OF THE COMPLEX RADICAL BY COAGULATION EXPERIMENTS.

By

ARUN K. DEY

Department of Chemistry, University of Saugar

and

S. P. MUSHRAN

Department of Chemistry, University of Allahabad

(Read at the annual meeting of the Academy on 22nd November, 1947)

ABSTRACT

Different samples of sodium argentothiosulphate have been prepared by alcoholic precipitation from a solution of silver halide (chloride or bromide) in a concentrated solution of sodium thiosulphate. The various properties of the isolated products have been studied. The results of analysis of the product gave the composition as : $Ag_2S_2O_3$, $4Na_2S_2O_3$, $2H_2O$, for all the samples. The valency of the complex ion was determined by coagulation of a positively charged ferric oxide sol with standard solution of the complex compound and by comparing the coagulation values with those for electrolytes of known valencies. The values showed that the complex radical was bivalent in character. On a systematic study of the formation of complex argentothiosulphates it has been concluded in an earlier communication, that only mono- and tri-valent complex anions are capable of existence in a solution of silver halide in sodium thiosulphate. On the other hand quantitative analysis leads to a formula which does not correspond with any of those already arrived at. The isolated product contains a much larger proportion of thiosulphate and it is therefore evident that the bivalency of the predominant ion thiosulphate is responsible for the abnormal coagulation values for the complex ion. It has been emphasized that in order to obtain a true formula of any co-ordination compound physico-chemical methods must be adopted as the formula obtained by isolation and subsequent analysis always include those of double salts and absorption complexes as well.

INTRODUCTION

It is well known that the removal of silver halide by sodium thiosulphate solution during fixation of photographic negatives involves the formation of complex compounds. The investigations of argento-thiosulphates have been of considerable interest and compounds of different compositions have been isolated from the solution by various workers. Mention may be made of the work of Baines[1], and Spacu Murgulescu[2] who analysed some samples and assigned formulae to the products. In an important communication[3] Basset and Lemon described the examination of the system $Na_2S_2O_3$--$Ag_2S_2O_3$—H_2O, at 25° and concluded the formation of the following complex compounds :

(i) $Na_3[Ag(S_2O_3)_2], H_2O$ or $3Na_2S_2O_3, Ag_2S_2O_3, 2H_2O$
(ii) $Na_5[Ag_3(S_2O_3)_4], 2H_2O$ or $5Na_2S_2O_3, 3Ag_2S_2O_3, 4H_2O$
(iii) $Na[Ag(S_2O_3)], H_2O$ or $Na_2S_2O_3, Ag_2S_2O_3, 2H_2O$
(iv) $Na[Ag_3(S_2O_3)_2], H_2O$ or $Na_2S_2O_3, 3Ag_2S_2O_3, 2H_2O$

The divergent results recorded in literature led us to investigate the formation of argentothiosulphate complexes and in a recent paper[4] we described our results on the compositions of such compounds studied by the solubility method[5] devolved by us, for elucidation of the formulae of complex compounds.

In this paper we have described the preparation and properties of sodium argentothiosulphate obtained by alcoholic precipitation from a solution of silver halide (chloride or bromide) in a concentrated solution of sodium thiosulphate The chemical composition has also been determined by quantitative analysis. Incidentally an attempt was made to determine the valency of the complex ion by the coagulation of a colloidal solution of positively charged ferric oxide, a method similar to that adopted by Ghosh and Dhar [6] for showing the bivalency the fluorideion.

EXPERIMENTAL

Preparation :—20 grams of 'AnalaR' silver nitrate was dissolved in water and silver halide was precipitated by the addition of either

'AnalaR' hydrochloric acid solution or a solution of chemically pure sodium bromide The precipitated silver halide was thoroughly washed free from the precipitating electrolytes and then dissolved in a concentrated solution of sodium thiosulphate of 'AnalaR' quality, care being taken to use the minimum quantity of sodium thiosulphate To the solution was added about 150 c c of absolute alcohol and the heterogeneous mixture shaken vigorously when a white emulsion appeared and later an oily liquid separated at the bottom of the vessel This oily liquid was separated by means of a separating funnel and received in an evaporating dish to which was then added a further quantity of alcohol On stirring with a glass rod, a white solid mass separated out The lumps were broken and washed thoroughly with alcohol and dried at a room temperature of about 30° It was found that the compositions of different samples, whether prepared from silver chloride or silver bromide, were the same and the properties were also similar

Properties —The product has a colourless appearance and is fairly soluble in water Hydrochloric acid separates sulphur from the compound, with brisk evolution of sulphur dioxide while silver chloride does not separate out Nitric acid behaves in the same way as hydrochloric acid, and on boiling a clear solution is obtained

The compound is readily soluble in ammonium hydroxide, and on adding nitric acid to the ammoniacal solution, some white particles separate out which change through a series of colours and finally become black This is probably due to the formation of silver sulphide from the complex When on aqueous solution is reacted with silver nitrate, silver in the complex gets perecipitated first as thiosulphate and finally changes to silver sulphide

The compound does not fuse on heating, but burns with a bluish flame and a black residue is left The compound does not darken on exposure to sunlight but an aqueous solution when exposed to solar light for six hours assumed a sky blue tinge Darkening of the solid occurs with time and it becomes dark grey in a period of about six

months. Similarly an aqueous solution, when kept for four months deposited silver mirror on the vessel.

The compound responds to the tests for thiosulphate, but the tests for silver are not obtained.

Analysis :—The analysis was carried out as described in the following lines ; Silver, thiosulphate and water of crystallisation were determined, while sodium was found by difference. The methods of analysis are given below.

Silver : —0.4 gram of the compound was weighed accurately and boiled vigorously with nitric acid to decompose the complex and thus a solution of silver nitrate was obtained. Silver was precipitated from the solution as chloride and estimated as usual.

Thiosulphate :—Thiosulphate was estimated by the method recently described by us[7]. 0.5 gram of the compound was accurately weighed dissolved in water and a solution of silver nitrate was added to it drop by drop with occasional stirring till precipitation was complete . The precipitate which was originally white gradually changed to yellow, red and finally became black, due to the conversion of silver thiosulphate to silver sulphide. The precipitate was filtered in a Gooch crucible, washed with water and the filtrate was concentrated to a volume of about 200 c.c. From the filtrate barium sulphate was precipitated by the addition of barium nitrate, and sulphate estimated. The Gooch crucible containing the silver sulphide precipitate was dried in an oven at 120°, till constant weight was attained. The total amount of sulphur contained in the complex was calculated from the weights of barium sulphate and silver sulphide :

$$\text{Total sulphur} = \text{Weight of silver sulphide} \times 0.12937 + \text{Weight of barium sulphate} \times 0.13738$$

From the weight of sulphur the amount of oxygen in $S_2O_3^{--}$ was calculated.

Water of crystallisation :—1 gram of the compound was taken in a watch glass, and heated to a constant weight in an air oven at 120°. The loss in weight gave the amount of water of crystallisation.

The average composition of the compound, arrived at by the analysis of a number of samples is given in table I.

TABLE I

	Found	Calculated
Silver	21.46%	21.69%
Sulphur	32.10%	32.13%
Oxygen (Calculated from the amount of sulphur)	21.08%	24.10%
Sodium (by difference) ...	18.66%	18.46%
Water of crystallisation ...	3.70%	3.62%
	100.00%	100.00%

Formula : $Ag_2S_2O_3$. $4Na_2S_2O_3$, $2H_2O$.

Coagulation experiments:—The determination of valency by the coagulation of solloidal solutions was first suggested by Freundlich,[8] and applied to show the bivalent nature of the fluoride ion by Ghosh and Dhar[6]. In this study a colloidal solution of positively charged ferric oxide was prepared by dispersing freshly precipitated hydrated ferric oxide by acetic acid, and purifying as usual by dialysis. The amount of ferric oxide in the sol was estimated by evaporating a measured volume to dryness, and finally heating strongly to a constant weight.

Concentration of the sol = 7·69 grams Fe_2O_3 per litre

For determining the coagulation values different amounts of the sol were taken in clean test tubes, and measured volumes of electrolytes were added. The time of observation was half an hour. The experiments were conducted at 25° and the total. volumes were kept 10 c.c. in every case.

Coagulation with electrolytes

TABLE II

Volume of electrolyte required

Volume of sol	M/5 KCl	M/400 K_2SO_4	M/1500 $K_3Fe(CN)_6$	M/2000 $K_4Fe(CN)_6$
1 cc	2 1 cc	0 5 cc	0 5 cc	0 4 cc
2 cc	2 8 cc	1 0 cc	1 0 cc	0 8 cc
3 cc	3 4 cc	1 4 cc	1 5 cc	1 2 cc

Coagulation with the complexes

TABLE III

Volume of sol	Volume of M/500 solutions of the complexes	
	Complex (1) from AgCl	Complex (2) from AgBr
1 cc	0 45 cc	0 40 cc
2 cc	0 80 cc	0 80 cc
3 cc	1 25 cc	1 20 cc.

From the above results we find that the coagulative power of the various electrolytes lie in the following order

$K_4Fe(CN)_6 > K_3Fe(CN)_6 >$ Complex (1) —Complex (2) $> K_2SO_4 >$ KCl

The coagulation values due to the complex ion lie near that of sulphate ion, thus showing the bivalency of the complex

DISCUSSION

It has already been said that a number of molecular compounds have been isolated from a solution of silver halide in sodium thiosulphate. Our results on the composition of these complexes (*loc. cit*) have conclusively proved that only two complex anions, viz., $[Ag(S_2O_3)]^-$ and $[Ag(S_2O_3)_2]^{-3}$ are capable of existence, their formation depending on the concentration of sodium thiosulphate solution used. With a concentrated solution of thiosulphate the reaction is :

$$AgX + Na_2S_2O_3 \rightleftharpoons Na[Ag(S_2O_3)]$$

when however, the thiosulphate concentration is lower, complex formation takes place according to the equation :

$$AgX + 2Na_2S_2O_3 \rightleftharpoons Na_3[Ag(S_2O_3)_2]$$

The compound $Na[Ag(S_2O_3)]$ was prepared by workers including Richards and Faber[9], Rosenheim and coworkers[10] and Baines (*loc. cit*), whereas $Na_3[Ag(S_2O_3)_2]$ was prepared, in comparatively recent years, by Spacu and Murgulescu (*loc. cit*). The other compounds reported by Basset and Lemon (*loc. cit*) seem to be double compounds or adsorption complexes, incorporating the two complexes with indefinite amounts of thiosulphate associated.

Our results described in this paper lead us to the formula : $Ag_2S_2O_3$, $4Na_2S_2O_3$, $2H_2O$, for the isolated product. On the other hand from the solubility results it is evident that the compound in presence of a higher concentration of thiosulphate should have been $Na[AgS_2O_3]$. It appears, therefore, that the isolated compound is an adsorption complex or a double salt. If the isolated compound would have been a true complex, the valency of the complex anion should have a value far greater than 4, The charge on the complex radical and thence its valency was determined by coagulation of a positively charged ferric oxide sol. The results indicate that the complex anion is bivalent, thus suggesting that this coagulation value is mainly due to the thiosulphate ion which is present in large excess, as a double salt or adsorption compound. It seems that some of the compounds isolated by Baines also belong to this type of compounds.

It should, therefore, be remembered that results obtained by methods of isolation and subsequent analysis are generally not very reliable, as they always include in their composition those of adsorption complexes and double salts as well. These complications are liable to mask the clear composition of the true co-ordination compounds formed. It is thus absolutely necessary that in addition to usual analysis physico-chemical methods must be adopted in order to elucidate the exact compositions of the complexes that may be formed.

References

1. Baines *Phot. J.*, 1929, **53**, 314; *J.C.S.*, 1929, 2763.
2. Spacu and Murgulescu *Zeit. anorg. Chem.*, 1932, **208**, 157.
3. Basset and Lemon *J.C.S.*, 1933, 1423.
4. Dey *Compt. Rend. Acad. Sci. U.S.S R.*, 1947., **50**, 1047
5. Dey *J. Ind. Chem. Soc.*, 1947, **24**, 207.
6. Ghosh and Dhar *Ibid.*. 1928, **5**, 203; *Koll. Z.*, 1928, **44**, 149.
7. Dey and Bhattachuya *J. Ind. Chem. Soc.*, 1946, **23**, 124.
8. Freundlich *New concepts in Colloid Chemistry*, London, 1926, 38.
9. Richards and Faber *Amer. Chem. J.*, 1899, **21**, 167.
10. Rosenheim and coworkers *Zeit. anorge. Chem.*, 1900, **25**, 74; *Ber.* 1928, **61**, 1731.

THERMAL IONIZATION OF CALCIUM AND DETERMINATION OF SPECIFIC CHARGE OF Ca^+.

By

A.S. Bhatnagar, M.Sc., D. Phil.

Physics Department, Allahabad University,

Now in C. S. I. R. laboratories, Delhi.

(Communicated by Dr. B. N. Srivastava, D. Sc.)

Abstract

The thermal ionization of calcium has been studied using the vacuum graphite furnace constructed by Saha and Tandon. The specific charge of Ca^+ has been determined by applying the space charge theory to positive currents under various potentials as explained in the paper on Lithium. The contribution of the terms $b(T)$ and $b'(T)$ for Calcium in the ionization formula tends to lower the effectiveionization potential. The mean value of the energy of ionization is 136·9 K. cals. The value of the specific charge of calcium is 7.5×10^{12} e. s. u./gm.

1. Introduction.

The Space charge theory for unipolar currents was developed by Srivastava and Bhatnagar (1944 a), and was applied by them (Srivastava and Bhatnagar, 1944 b) to determine the e/m for electrons from graphite In a subsequent paper (Srivastava and Bhatnagar 1946) the theory was applied to determine the specific charge of Li^+ using a strong magnetic field to deflect off the electrons and obtaining thereby, an effectively unipolar positive current; the e/m for the positive particle is then obtained from the relation giving the variation of the positive current with voltage applied to the Faraday cylinder.

In the present paper the same method has been employed to determine the specific charge of Ca^+. A study of the thermal ionization of Calcium has also been made, the elements barium and strontium of the same group, having been studied by Srivastava (1940 a 1940 b).

2. THERMAL IONIZATION OF CALCIUM.

A detailed description of the apparatus and the experimental procedure has been given by Srivastava in his paper on strontium. Srivastava 1940 b

Due to high ionization potential of calcium (6.02 eV) the temperatures at which measurable ionization could be produced in the graphite furnace was higher than hitherto employed in similar experiments. The side-furnace which contains the metal was modified to develop a temperature at which calcium has enough vapour pressure to produce appreciable ionization Existing data on the vapour pressure of calcium show that, in the region of the temperature range at which the present measurements have been made, values of the vapour pressure of calcium are not available The following procedure had, therefore, to be adopted to get the values of the vapour pressure at the different temperatures used in the experiments.

There are two sets of data available, one for solid state givenby Rudberg (1934) and the other for liquid state by Ruff and Hartmann 1924) The data on the solid state are at lower and those on the liquid state are at higher temperatures than those in our experiment Therefore, to get the values of vapour pressure for our range of temperature the solid state data have beenextrapolated to the melting point of calcium, and similarly, the data on the liquid state have been extrapolated downwards to the melting point The difference between the slopes of the curves so obtained agrees well with the latent heat of fusion of calcium (cf. Srivastava's paper on strontium) and shows that the values of the vapour pressure for higher temperatures, as read from the vapour pressure curve for solid state by extrapolating it to the melting point can be taken as correct. As a further check the value of the vapour presure has also been calculated from the formula

$$\log p(\mathrm{mm}) = -\frac{9670}{T} + 8.15,$$

as given by Rudberg

The calculated values agree well with those obtained by graphical extrapolation A mean of these two values has been utilized to

get the vapour pressure in the side tube containing calcium Knowing the value of the vapour pressure p in the side tube at temperature T the value of vapour pressure p at temperature T in the main furnace is calculated from the relation

$$p/p = \sqrt{T/T}$$

Like barium and strontium for calcium also the contribution of the terms b T and b T occurring in the ionization formula

$$\log K = \log \frac{p_i}{p_a} \frac{p_e}{p_a} \quad \frac{U}{4.573T} + \frac{5}{2}\log T \quad (6.494 + \log g)$$

$$+ \log b(T) + \log b'(T) \qquad (1)$$

where the pressures are expressed in atmospheres is such that it tends to lower the effective energy of ionization—a fact which accounts for the occurrence of calcium in a highly ionized degree in the sun whereas other elements with much higher ionization potential are much less ionized The values for the case of calcium as calculated from the energy states given by Bacher and Goudsmidt are

$$b(T) = 1.00029 \text{ at } 2063 \text{ K}$$
$$b'(T) = 2.00097 \text{ at } 2063 \text{ K}$$

Thus throughout the temperature range of our experiment we can assume $b(T) = 1.00$ and $b'(T) = 2.00$ and the ionization formula (1) becomes

$$\log K = \frac{U}{4.573T} + \frac{5}{2}\log T - 6.479 + \log 2 \qquad (2)$$

and K from the theory of the experiment is given by (see Srivastava 1940*a*)

$$K = \frac{2\pi kT}{e^2 S^2}\left(\frac{r^2+d^2}{r^2}\right)^2 \frac{i_g^+ \; i_g^-}{p_a} \sqrt{m_i \times m_e} \; (1.013 \times 10^6) \qquad (3)$$

where r = the radius of the aperture in limiting diaphragm

d = distance between the diaphragm and the effusion hole

S = area of the effusion hole

i_g^- and i_g^+ are the negative and positive currents respectively and all other quantities have their usual significance

The values of the currents i_g^- and i_g^+ occurring in the table are the zero-field values of the current obtained as explained in the paper on thermionic work fuction of graphite (Bhatnagar 1944).

Table I gives the results on the thermal ionization of calcium in the temperature range 1898°K to 2063 K The mean value for the energy of ionization comes out to be 136 9 K cals which agrees with the spectroscopically determined value 139 K cals within limits of experimental error

TABLE I

Diameter of effusion hole = 1 008 mm
Distance between effusion hole and diaphragm = 14 5 mm
Sensitivity of the galvanometer = 1 25 × 10^{-7} amp/mm
Radius of limiting diaphragm aperture 4 2 mm

Mean Temp of the graphite furnace K	Temp of aux furnace K	log p_{ca} mm in aux fur	log p_{ca} mm in main fur	i_g^- mm	i_g^+ mm	log k (atmos)	U in K Cals
2063	1037	$\bar{2}$ 7[illegible]	$\bar{2}$ 9041	156 100	53	$\bar{13}$ 7291	138 7
1973	1047	$\bar{2}$ 913	$\bar{2}$ 9833	[illegible] × 100	34	$\bar{13}$ 1023	137 7
1960	1047	$\bar{2}$ 913	$\bar{2}$ 9833	80 100	30	$\bar{13}$ 0933	137 6
1955	1047	$\bar{2}$ 913	$\bar{2}$ 982	80 × 100	33	$\bar{13}$ 1312	136 8
1949	1047	$\bar{2}$ 913	$\bar{2}$ 9820	80 × 100	24	$\bar{14}$ 9952	137 7
1942	1022	$\bar{2}$ 630	$\bar{2}$ 7705	80 100	27	$\bar{13}$ 2563	134 6
1931	1027	$\bar{2}$ 675	$\bar{2}$ 8132	80 × 100	30	$\bar{13}$ 2569	133 9
1917	1027	$\bar{2}$ 675	$\bar{2}$ 8117	106 × 30	15	$\bar{14}$ 5536	139 1
1896	1002	$\bar{2}$ 440	$\bar{2}$ 5797	41 × 30	11	$\bar{14}$ [illegible]66	135 7
1828	982	$\bar{2}$ 255	$\bar{2}$ 3899	58 × 30	2	$\bar{15}$ 8155	137 6

2. Determination of e/m

It has already been explained in our paper on the space charge effect that the specific charge of the particle carrying the current can be determined by applying the Space Charge theory provided the current is unipolar. This condition is experimentally realised by deflecting, with the help of a strong electromagnet, the electrons from the beam of the charged particles effusing out of the tiny hole in the graphite furnace and, thus preventing them from entering the inter-electrode space which, in our case, is formed by the diaphragm and the Faraday cylinder. The heavy ions (Ca^+) are little affected by the magnetic field and pass through the limiting diaphragm, and are collected by the Faraday cylinder to which a suitable negative potential is applied. The current produced by the charged particles is measured at various potentials on the Faraday cylinder. Table II gives a typical set of observations.

The relation between the current and the applied voltage on taking space charge effect into account is (Srivastava 1946)

Table II

V in Volts	d^+ in mm
0.5	3·5
1	4·5
1.2	5
1.5	6
1.8	6 5
2	7
2 5	8
3	9
4	12
5	13 5

$T = 1793°$, $x = 2.1$ cm., $A = \pi \times (.42)^2$, Gal. sens. $= 1.25 \times 10^{-9}$ amp/mm.

$$i = \frac{\nu^2}{9\pi}\left(\frac{e}{m}\right)^{\frac{1}{2}} \frac{V^{3/2} \times A}{x^2} \quad \text{approx} \tag{4}$$

where x = distance between the diaphragm and the Faraday cylinder
A = area of the aperture in the diaphragm

Plotting i against V see Fig 1 e/m for the Ca^+ ion can be obtained from the slope of the curve The value so obtained is $e/m = 7.5 \times 10^{12}$ e s u/gm which agrees very closely with the calculated value for calcium taking for the value of electronic charge and for m the mass of Ca atom

This also identifies the particle producing positive currents in the experiments on the thermal ionization of calcium with Ca^+

The error likely to occur in the value of e/m obtained by this method has been discussed by Srivastava (1946) and is about 15%

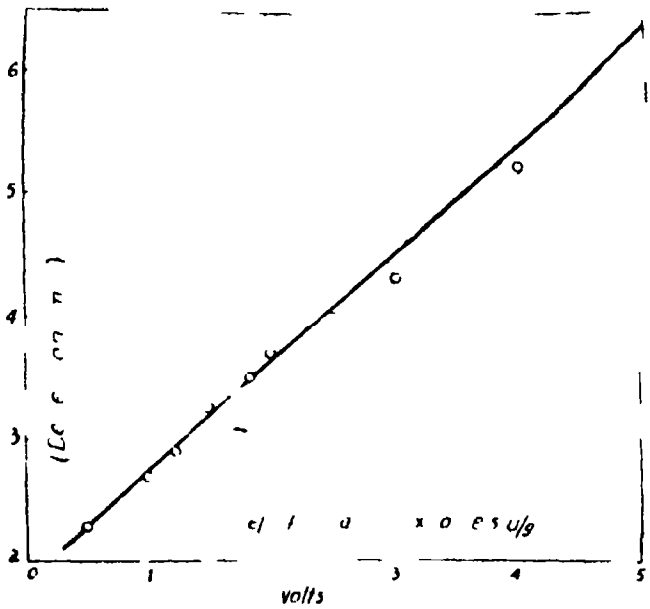


Fig 1

My best thanks are due to Dr B N Srivastava, D Sc under whose guidance the work was done at the University of Allahabad

References

1. Bacher, R. F. and Goudsmidt, S. 1932 *Atomic Energy States* 1st ed.
2. Bhatnagar, A. S. 1944 *Proc. Nat. Acad Sci. India* **A.** 14, 5
3. Rudberg 1934 *Phys. Rev.* 46, 763.
4. Ruff and Hartmann 1924 *Zs. anorg. Ch.* 133, 29.
5. Srivastava B. N. and Bhatnagar A. S., 1944a *Proc. Nat. Acad. Sci. India* ,**14, 106.**
6. — 1944 b, *Ibid*, 14, 118
7. — 1946, *Ibid*, 15, 175.
8. Srivastava B. N. 1940a *Proc. Roy. Soc.* A. 960, 175, 26
9. — 1940b, *Ibid* A. 176, 343.
10. 1946 *Proc. Nat. Acad. Sci. India* 15, 165

67487

INDIA 28 JUL 1961 NEW DELHI

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1947

PART III] SECTION A [VOL 16

THERMAL IONIZATION OF ALUMINIUM AND DETERMINATION OF THE SPECIFIC CHARGE OF Al^+

By

A S BHATNAGAR M Sc D Phil

PHYSICS DEPARTMENT ALLAHABAD UNIVERSITY

NOW IN C S I R LABORATORIES DELHI

(Communicated by Dr B N Srivastava D Sc)

ABSTRACT

The thermal ionization of Aluminium has been studied employing the vacuum graphite furnace constructed by Saha and Tandon The problem is experimentally more difficult than for other elements due to the low vapour pressure and large ionization potential of aluminium and has necessitated some modification in the usual experimental arrangement The mean value of the energy of ionization is found to be 135 9 K cals which is in good agreement with the spectroscopically determined value within limits of experimental error

Following the method developed in the paper on lithium the e/m for Al^+ has also been determined by applying the space charge theory to unipolar positive current produced by Al^+ ion The value obtained is $1\ 22 \times 10^{13}$ e s u /gm

I INTRODUCTION

In the present paper the thermal ionization of aluminium has been studied and the specific charge of Al^+ determined Similar studies were made with Lithium (Srivastava and Bhatnagar 1946) and calcium (Bhatnagar 1947) A full account of the apparatus

used for the study of thermal ionization has been given by Srivastava (1940). In order to determine the specific charge a strong electromagnet has been recently included in the apparatus. A complete description of the electromagnet, of the experimental procedure for determining the specific charge of ions, and of the theory underlying the method is given in the paper on lithium, (Srivastava and Bhatnagar 1946).

The method is applicable only to unipolar currents, i.e., the currents produced by one type of charged particles. This condition is experimentally realised by deflecting away the electrons from the effusion beam, with the help of the electromagnet. The method gives very satisfactory results, and helps in the identification of the particles producing positive currents in the study of the thermal ionization of elements.

2. Thermal Ionization of Aluminium

The problem has greater experimental difficulties than hitherto encountered in our study on the thermal ionization of elements due to the fact that aluminium has a very low vapour pressure and even at temperatures as high as 1500°K of the container in which the element is placed during the experiment, no measurable ionization was produced in the main furnace. After a large number of

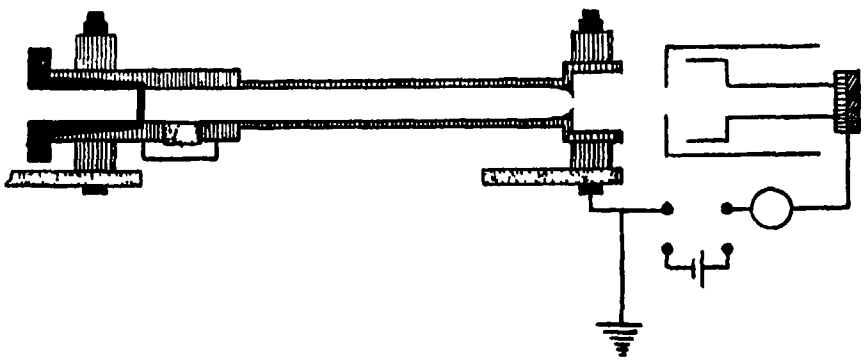


Fig. 1.

trials, it was found that no separate side-tube attached to the main furnace and heated by conduction from the latter, as has been employed so far in all previous experiments, could produce the required temperature. The side furnace was, therefore, dispensed with and in its place, a small plug (see fig 1) with a shallow cavity in its neck was screwed on to the main furnace such that the substance contained in the cavity was in level with the walls of the main furnace and had the same temperature as that part of the graphite tube

This portion of the tube is at a lower temperature than the central part of the graphite furnace, but is incandescent enough to enable its temperature to be read with the pyrometer, which has been throughout employed to find the temperature of the main graphite furnace. Aluminium in the form of fine powder was introduced in the cavity at the top of the plug which was then screwed on to the main furnace

The ionization currents produced by electrons and the positive ions were measured at various temperatures and the corresponding equilibrium constant K calculated with the help of the following relation (See Srivastava 1938 eqn. 15)

$$K = \frac{2\pi kT}{e^2S^2}\left(\frac{r^2+d^2}{r^2}\right)^2 \frac{i_q^- i_q^+}{p_a} \frac{\sqrt{m_i}}{1{\cdot}013\times 10^6} \cdot \cdot \quad (1)$$

where r = the radius of the aperture in the limiting diaphragm.

d = the distance between the effusion hole and diaphragm

S area of the effusion hole and all other quantities have their usual significance

The ionization formula

$$\log K = \log \frac{p_i \times p_e}{p_a}$$

$$= -\frac{U}{4.573T} + \tfrac{5}{2}\log T - 6{\cdot}479 + \log 2 + \log b'(T) - \log b(T), \quad (2)$$

with the help of (1) then gives U, the energy of ionization per gram atom. The term $b(T)$ comes out to be 2·0000 and $b'(T) = 1\ 0000$

The available data on the vapour pressure of aluminium fortunately cover the range of temperature over which observations have been taken in these experiments.

Table I gives the results on the thermal ionization of aluminium. i_g^- and i_g^+ in columns 4 and 5 are the zero-field values of the current obtained as explained in the paper on thermionic work function of graphite (Bhatnagar, 1944). The value of the energy of ionization so obtained agrees well with the spectroscopically determined value.

TABLE I

Radius of effusion hole = 0·8 mm.
Radius of the aperture in the limiting diaphragm = 4.2 mm.
Distance of diaphragm from effusion hole = 18 mm.
Sensitiveness of galvanometer = $1{\cdot}25 \times 10^{-7}$ amp. mm.

Temp. of graphite furnace T (Abs)	Temp. of Aux. furnace T (Abs)	log p in main furnace	i_g in mm	i_t in mm	log K (Atmos)	U in K cals
1840	1660	1·2223	1500	15	15·7373	131·2
1850	1665	1·2479	1530	30	16·2424	137·4
1863	1675	1·3731	2010	56	15·8142	135·3
1878	1683	1·3987	2280	65	15·9112	135·6
1903	1705	1·5233	4200	83	14·1639	135·3
1908	1705	1·5244	3600	80	14·0810	136·4
1930	1725	1·6244	5100	95	14·2120	136·9

3. Determination of e/m

After the aluminium has been ionised in the main furnace, the products of ionization consisting of electrons and ionised atom effuse out of the effusion hole. The electrons are deflected off from the effusing beam by the electromagnet, as they traverse the path between the effusion hole and the limiting diaphragm, and only the positive ions, which are very little affected by the magnetic field, enter the space between the diaphragm and the Faraday cylinder The positive ions are collected by the Faraday cylinder which is maintained at a suitable negative potential, and the flow of the positive ions from the diaphragm to the Faraday cylinder constitutes the unipolar positive currents to which the space charge theory may be applied. The currents are measured at various accelerating voltages (see table II) and are given by the relation (Srivastava 1946)

$$i = \frac{\sqrt{2}}{9\pi}\left(\frac{e}{m}\right)^{1/2} \frac{V^{3/2}}{x^2} A \text{ approx.} \qquad . \quad . \quad (3)$$

where x = the interelectrode distance, i.e., the distance between the diaphragm and the Faraday cylinder, and A = the area of the aperture in the limiting diaphragm.

TABLE II

$T = 1850°$ K, $x = 21$ mm, $A = \pi\ (0{\cdot}12)^2$ sq cm

V in volts	d in mm
5	29
1·0	34
1·3	35
1·6	36·5
2·0	39
2·5	41
3·0	44
4·0	49·5
5·0	52

Plotting $i^{2/3}$ against V we get the curve of Fig. 2. The slope of the curve which is equal to

$$\left[\frac{\sqrt{2}}{9\pi}\left(\frac{e}{m}\right)^{1/2}\frac{A}{r^2}\right]^{2/3}$$

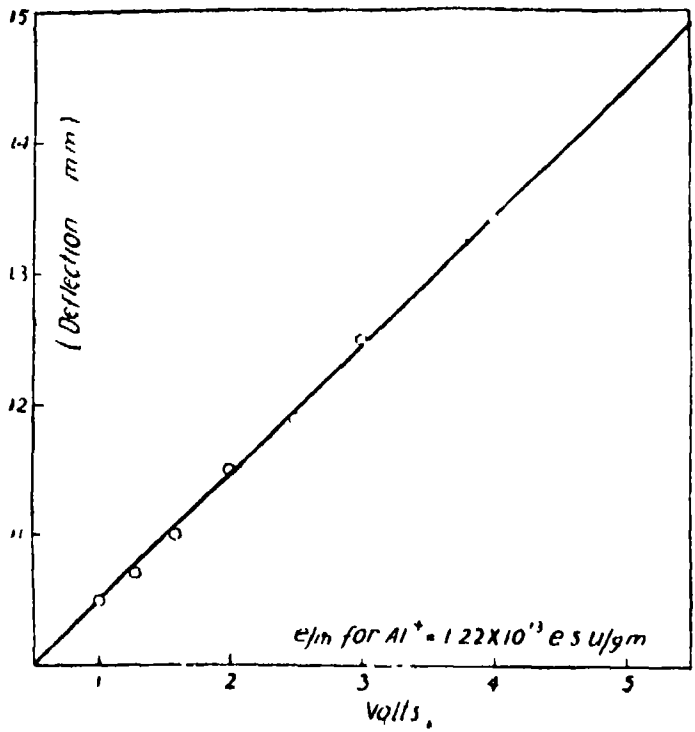


Fig. 2.

from equation (3) then enables us to calculate e/m. The value of e/m so calculated is 1·22 e.s.u./gm which agrees well with the value for Al^+ obtained by direct calculation and establishes beyond doubt that the positive current in the experiment on the thermal ionization of aluminium is due to $Al.^+$ As shown by Srivastava (1946) this method is capable of yielding values of e/m correct to about 15%.

My sincere thanks are due to Dr. B. N Srivastava, D Sc., under whose guidance this work was done at the University of Allahabad.

References

Bhatnagar, A. S. (1947), *Proc. Nat. Acad. Sci.* India, 17, 45.

Bhatnagar, A. S. (1944), *Proc. Nat. Acad. Sci.* India, A 14, 5.

Srivastava, B. N. (1938), *Proc. Nat. Inst. Sci* India. 4, 365.

Srivastava, B. N. (1940), *Proc. Roy. Soc. Lond.* 175, 26 ; 176, 343.

Srivastava, B. N. (1946), *Proc. Nat. Acad. Sci.* India, 15, 65.

Srivastava, B. N. and Bhatnagar A. S. (1946), *Proc. Nat. Acad. Sci.* India, 15, 175.

STUDY OF THE COMPLEX FORMATION BETWEEN MERCURIC CHLORIDE AND SOLUBLE CHLORIDES BY THE ELECTRICAL CONDUCTIVITY METHOD

PART II STUDY OF THE $HgCl_2$ KCl SYSTEM

By

ARUN K. DEY

Department of Chemistry, University of Saugar

(Read at the Annual Meeting of the Academy on 22nd November, 1947)

ABSTRACT

In part I of the series, the compositions of chloromercuric acids have been studied by the electrical conductivity method. In this paper the compositions of chloromercuriates, resulting in the complex formation between mercuric chloride and potassium chloride have been described. The method adopted for the study is the same as followed by the author for the study of various complex forming systems The conductivity curves give indications of the formation of the following complex compounds: KCl, $HgCl_2$; 2KCl, $HgCl_2$ and 4KCl, $HgCl_2$.

INTRODUCTION

A large amount of work has been carried on the nature of the complex mercuric compounds. In recent years Bhagwat and Toshniwal[1] investigated the behaviour of mercuric chloride in aqueous solutions. Yajnik and Uberoy[2] adopted some physico-chemical methods for the study of complex formation between mercuric salts and soluble halides, and Pernot[3] and Gallais[4] studied the complex formation in non-aqueous solvents. Samuel and co-workers[5] studied the complex system by spectroscopy and Nayar and Saraf[6] investigated the Raman Spectra. Some of the workers are in favour of assigning the formula R_2HgX_4 to the complex formed, whereas others favour HgX^-_3 as the formula for the complexion. Thus Krishnamurti[7],

Braune and Engelbrecht[8] and Bernstein and Martin[9] are in favour of the latter formula for the complex On the other hand Solanki and Joshi[10] by conductivity, viscosity and refractivity measurements claim to have obtained the evidence for the existence of the following compounds 10KI, $HgCl_2$, 20KI, $HgCl_2$ and 4 5KI, $HgCl_2$, which however have not been confirmed by other workers

In view of the conflicting results obtained by various workers we undertook the study of this problem and in Part I of the series[11] we have investigated the complex formation between mercuric chloride and hydrochloric acid In this paper the work has been extended to the study of mercuric chloride-potassium chloride system.

EXPERIMENTAL

Specific conductivity values for solutions of M/200 mercuric chloride of different concentrations of potassium chloride and also for mixtures of various compositions were accurately determined at 30°

The experimental results are given in the following tables

Electrical conductivity of M/200 mercuric chloride = 6 343 × 10^{-6} mhos

TABLE I

Specific conductivity of potassium chloride at different dilutions

Concentration	Electrical conductivity in 10^{-3} mhos
M/10	12 84
M/20	6 863
M/30	4 792
M/40	3 537
M/50	2 856

Concentration	Electrical conductivity in 10^{-3} mohs
M/60	2·120
M/70	2·096
M/80	1·798
M/90	1·713
M/100	1·416
M/110	1·329
M/120	1·237
M/140	1·014
M/160	0·9282
M/180	0·8078
M/200	0·7356
M/240	0·6326
M/280	0·5462

TABLE II

Specific conductivity of mixtures of mercuric chloride and potassium chloride of various compositions

Final concentrations of the constituents in the mixture		Ratio		Specific conductivity in 10^{-3} mhos
$HgCl_2$	KCl	$HgCl_2$	KCl	
M/200	M/1	1	200·0	13·074
,,	M/20	1	10·0	6·975

Final concentrations of the constituents in the mixture		Ratio	Specific conductivity in 10^{-3} mohs
$HgCl_2$	KCl	$HgCl_2$: KCl	
M/200	M/30	1 : 6.67	4.856
,,	M/40	1 : 5.00	3.585
,,	M/50	1 : 4.00	2.961
,,	M/60	1 : 3.33	2.552
,,	M/70	1 : 2.86	2.120
,,	M/80	1 : 2.50	1.816
,,	M/90	1 : 2.22	1.749
,,	M/100	1 : 2.00	1.465
,,	M/110	1 : 1.82	1.342
,,	M/120	1 : 1.67	1.249
,,	M/140	1 : 1.43	1.027
,,	M/160	1 : 1.25	0.9425
,,	M/180	1 : 1.11	0.8221
,,	M/200	1 : 1.00	0.7579
,,	M/240	1 : 0.83	0.6419
,,	M/280	1 : 0.71	0.5545

DISCUSSION OF RESULTS

It is well known that the physical properties of mixtures not yielding complexions are additive. The converse is also true and any change in the physical properties of mixtures is usually due to complex forma

tion. From the experimental data recorded in this paper the percentage change in electrical conductivity due to the complex formation between mercuric chloride and potassium chloride have been tabulated below.

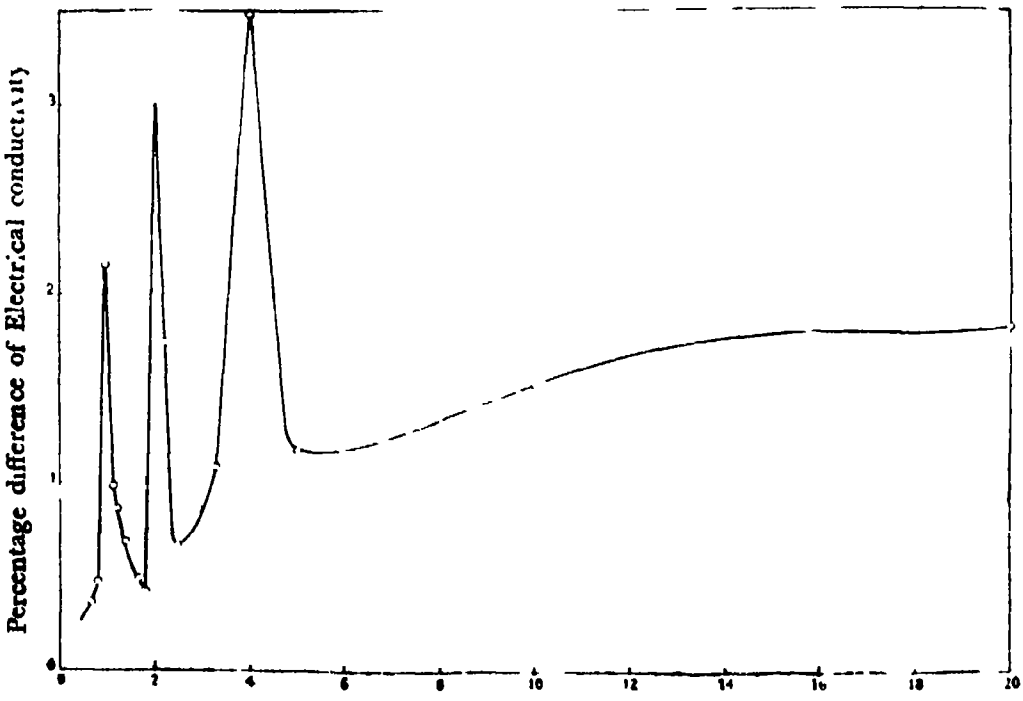
TABLE III

Mixtures of mercuric chloride and potassium chloride

Composition of the mixture $HgCl_2$: KCl	Sum of the conductivities of the constituents in 10^{-3} mhos	Observed conductivity of the mixture in 10^{-3} mhos	Difference in 10^{-4} mhos	Percentage difference
1 : 20.0	12.84	13.074	2.31	1.81
1 : 10.0	6.869	6.973	1.04	1.51
1 : 6.67	4.798	4.856	0.58	1.21
1 : 5.00	3.543	3.585	0.43	1.18
1 : 4.00	2.862	2.961	0.99	3.46
1 : 3.33	2.426	2.552	0.26	1.07
1 : 2.86	2.102	2.120	0.18	0.86
1 : 2.50	1.804	1.816	0.12	0.66
1 : 2.22	1.719	1.749	0.30	1.74
1 : 2.00	1.422	1.465	0.43	3.02
1 : 1.82	1.335	1.342	0.07	0.42
1 : 1.69	1.243	1.249	0.06	0.48
1 : 1.43	1.020	1.027	0.07	0.69
1 : 1.25	0.9345	0.9425	0.08	0.86
1 : 1.11	0.8141	0.8221	0.08	0.98
1 : 1.00	0.7419	0.7579	0.16	2.15
1 : 0.83	0.6389	0.6419	0.03	0.47
1 : 0.71	0.5525	0.5545	0.02	0.36

From the above table a graph has been plotted with percentage difference in conductivity against the composition of the mixture The curve shows sharp breaks corresponding to the following compositions of the mixture : 1KCl, 2KCl and 4KCl for 1 molecule of $HgCl_2$. Thus we conclude that the following chloromercuriates are formed by complex formation between mercuric chloride and potassium chloride : KCl, $HgCl_2$; 2KCl, $HgCl_2$ and 4KCl, $HgCl_2$. It will be of interest to remember that in Part I, similar complexes were found to be present in a mixture of mercuric chloride and hydrochloric acid solutions. Some workers have reported the formation of a compound 1/2KCl, $HgCl_2$, which was not found by us, as we did not work with extremely dilute solutions of potassium chloride. It is likely that this compound may also exist under suitable conditions.

Conductometric Study of $HgCl_2$ KCl System



Values of the fraction · conc. of KCl/conc $HgCl_2$

From these studies, I am of opinion, that since several well defined compounds are capable of existence, involving various proportions of mercuric chloride and potassium chloride the wide variation in the compositions of these complexes as found by different workers is quite likely, as their products may easily be a mixture of one or more of such complexes

Reference

1 Bhagwat and Joshiniwal *J Ind Chem Soc*, 1942 **19** 493

Yajnik and Uberoy *J Ind Chem Soc* 1941 **46** 802

3 Pernot *Compt Rend* 1927 **185** 950 *Ann Chim* 1931 **15** 5

4 Gallais *Compt Rend* 1932 **195** 75

5 Nayar and Sarat *J Ind Chem Soc* 1943 **20** 314

6 Samuel and coworkers *Ind J Phys*, 1935 **9**, 491

7 Krishnamurti *Ibid*, 1931, **6** 7

8 Braune and Englebrecht *Z phys. Chem*, 1930, **11B** 409

9 Bernstein and Martin *Trans Roy Soc*, Canada, 1937, **34**, (iii), 95

10 Solanki and Joshi *J Ind Chem Soc*, 1942, **49**, 9

11 Dey and Bhattacharya *Proc Nat Acad Sci*, India, 1947, **16A**, 1

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES INDIA
1948

PARTS I & II] SECTION A [VOL. 17

CONTENTS

PART I

PAGE

1. Chemical Examination of Root bark
By M P. Singh and J.D. Tiwari 1

2. Oxidation of Sulphur
By N R Dhar and B V S Raghavan 7

3. Synthesis of Higher dibasic Acids Part I
By L.D. Tiwari and J. D. Tiwari 11

4. Synthesis of Higher dibasic Acids Part II
By L D. Tiwari and J D. Tiwari 19

5. Comparative Experiments with Inorganic and Organic Manures
By N R. Dhar and B G. Chatterjee 27

Continued on the fourth page of the cover

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India): Rs. 5/8 (Foreign)

67488

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES INDIA
1948

PART III] SECTION A [VOL 17

CONTENTS

Page

1 A Note on High Frequency Current Density in a Hollow Cylindrical Conductor
By Santi Ram Mukherjee 69

2 Preparation and Study of Thorium Borate Jellies
By S P Mushran 73

3 Intensity Variations of Radio Signals and their bearings on Diversity Reception
By Ram Neti Singh 83

4 Studies in the nature of Hydrated Ferric Oxide Part II Adsorption of various ions by the Hydrated Oxide in Acidic Alkline and Neutral Media
By Arun K Dey & Satyeshwar Ghosh 93

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) Rs 5/8 (Foreign)

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1948

PART IV] SECTION A [VOL. 17

CONTENTS

PAGE

On the Rational Solution of the Diophantine Equation $a(x^{m-1}-1)-b(y^{n-1}-1)=z^{p-1}$.

By D. P. Banerjee 101

New Lines in Carbon Spectrum.

By A. S. Varma 103

Strazzeri's Formula in Rectilinear Congruences and its Applications.

By Ram Behari and Ratan Shanker Mishra 109

Note on Conics of Double Osculation of a Cubic.

By Haridas Bagchi 115

ALLAHABAD
PUBLISHED BY THE COUNCIL
Price Rs. 5 (India): 5/8 (Foreign)

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1948

PARTS V & VI] SECTION A [VOL. 17

CONTENTS

PAGE

On the Bending of an Elliptic Plate under certain Distributions of load. (ii)
By H M Sengupta 143

Note on Circular Cubics and Bicircular quartics
By Haridas Bagchi 169

Motion in Fluids of variable density and varying Coefficient of Viscocity
By Santi Ram Mukherjee 185

ALLAHABAD
PUBLISHED BY THE COUNCIL
Price Rs. 5 (India): 5/8 (Foreign)

CHEMICAL EXAMINATION OF THE ROOT-BARK OF ALANGIUM LAMARCKII

By

M. P. Singh and J. D. Tewari

The plant Alangium Lamarckii belongs to the Natural Order Cornaceae and is reported to possess important medicinal properties. The part mostly used as medcine is the root-bark which is up to 2 mms. thick, brittle and dark brown in colour and highly bitter. Leaves and fruits also find use in medicine. The root-bark is described in the *Nighantu* as bitter, mucelaginous pungent, aperient; it expels worms, wind, phlegm and poison. The leaves are used externally to relieve rheumatic pains, and the fruits internally to cure phthisis and skin diseases.

From personal experience Sheriff (i) states that the bark is a good substitute for Ipcacuanhe, and proves useful in all cases in which the latter is indicated, except dysentery. It is given in syphilis and leprosy; the native consider it to be alexiteric abxiteric, especially in cases of bites from rabid animals. Dey. (2) reports its usefulness in simple continued fever. Chark, Sharang-Dharsamhita and Bhava-prakasha describe it as an antidote to snake venom.

The presence of a noncrystallisable alkaloid, provisionally named Alangine was reported by Dymock, (3) as far back as 1891. Later on, in in 1893, a reference of the same appeared in Chemisches Zentralblatt (4). Chopra in 1933. (5) submitted the drug to detailed chemical study. He says, " Detailed chemical examination revealed the presence of an alkaloid and fair amount of Potassium chloride, but no tannins or glucosides. The base was purified to a great extent but all attempts to prepare a crystalline salt have thus far failed. The sulphate of the base was obtained as a white powder which was found to be hygroscopic and had a tendency to turn yellow on keeping."

Neither the alkaloid nor any one of its salts have so far been obtained in a crystalline form. It had not been possible even to decide whether the alkaloid was a single compound or a mixture of others, differing but slightly in their chemical and physical properties. The presence of characteristic groups and the nature of the nitrogen atom in the molecule of the alkaloid too, had not been studied.

In this series it is intended to throw more light on the above mentioned points. The present study was already in progress when a paper by Dutt and Parihar (6) appeared, giving results of their investigations on the drug. They report the presence of a single alkaloid—Alangine—to which they have assigned the formula $C_{11}H_{25}O_2N$,—(M.P.205–08°C. with decom.) A number of the salts of the alkaloid with their melting points are given. A few colour reactions are also given. The authors have given no reference of the previous work in the field. The colour reactions and the molecular weight that they have found out are quite different from those given by Dymock. The present authors have isolated three different alkaloids-two isomeric with each other, and a third different from these two; from the same drug, and have provisionally named them (i) Alangine A, (ii) Alangine B, and (iii) Alanginine. It is very probable, therefore, that the Alangine either of Dymock or Dutt and Parihar, is but a mixture and not a pure single individual compound. This is further supported by the fact that ethylacetate in which all the three alkaloids isolated by us, are soluble, has been used near the final stage of extraction by Dutt and Parihar. Naturally the precipitate that they obtain by adding a mixture of ether and petroleum ether (2:1) to the concentrated ethylacetate extract must also be a mixture of all three alkaloids. In the final stage of purification, the use of chloroform by them, in which solvent also all the three alkaloids are soluble, leave no room for doubt that they are dealing with a mixture and not a pure substance. The following table gives the values obtained by Dymock, present authors and Dutt and Parihar:—

Authors	Mol. wt.	M P.	C%	H%	N%	Dumas	N% Kheld. hls.	OCH_3%	Molecular formula.
(1) Dymock	266			..		..	..	..	..
Dutt and Parihar	291	205°—08°	76 25	8·36	.	4 68	4·68	10·36	$C_{16}H_{25}$ —O_2N.

(3) Present Author.

(i) Alangine A	..	353	219°	-20°	72·27	7·30	8 34	4·21	17.54	$C_{21}H_{2}O_3N_2$
(ii) Alangine B		353	105°	07°	72 20	7 41	8 18	4·15	17·49	$C_{21}H_{2}O_3N_2$
(iii) Alangimine	.	.	245°	47°	73 56	8 46	.	..		..

Furthermore the difference between the percentages of nitrogen determined by the Dumas and the Kjeldahl's methods show that in the molecule of the alkaloid nitrogen exists in two different forms and the possibility of a ring nitrogen is consequently inferred. Such a difference is not recorded by Dutt and Parihar.

Experimental

Preliminary assay of the root-bark revealed the presence of about ·91% of an alkaloid on the air dried material. 25 gms. of the air-dried root-bark was successively extracted with the following solvents:—

1. Petroleumether (40°—60°): —A dark brown viscous oily substance ·45% was obtained.
2. Absolute ether:—A dark brown viscous oily substance ·84%.
3. Absolute alcohol: —A dark brown hygroscopic mass 5·7%.
4. Alcohol 70%: —12·15%.

Isolation:—

10 lbs. of the air dried root-bark was finely powdered and extracted with a cold homogeneous mixture of 90 parts ether, 10 parts alcohol, and 2 parts liquor ammonia, the final percolation being done after stirring up the drug with some alcoholic ammonia The percolates were individually treated with dry hydrochloric acid gas in the cold and the ethereal solution decanted off from the precipitated hydro-

chlorides of the bases, ammoniated with liquor ammonia and used for subsequent percolation. After three percolations the ethereal solution was made ammoniacal and then just acidic with acetic acid and ciher distilled off on the waterbath for fresh use. From the residue left behind, the residual base was recovered by removing fatty matter with petroleumether (40°—60°c) and dissolving out the salts with cold and finally with some warm water. The combined hydrochlorides got from the different percolates and the aqueous solutions of the salts of the residual alkaloids were mixed together, the base precipitated with sodium carbonate (1%) and shaken out with chloroform. The chloroform layer was allowed to stand for 24 hours, filtered and shaken out with 1% oxalic acid till in the last extract no precipitate was obtained by adding Meyer's reagent. From the solution of the oxalates thus obtained the bases were fractionally precipitated with ammonia shaken out with ether and three fractions collected after rationally missing the different initial fractions according to their basic solutions thus obtained were dried over anhydrous sodium sulphate strengths. The three ethereal and concentrated to a small volume over a waterbath at 50°c. A light brown solid seperated in all the three and was collected over a filter paper, washed a few times with dry ether and stored as fraction A. From the respective mother liquors on largely diluting with petroleum ether a deep yellow substance was obtained and was named fraction B. The fractions A and B were further purified by repeating the above treatment and finally by dissolving them separately in dry acetone which did not dissolve a very small crop of a cream coloured substance (M. P. 245°—47° with decomposition). The acetone was removed, the solids dissolved separately in dry ether, the ethereal solution concentrated to a small volume and the base precipitated by adding large volume of petroleum ether. The three substances were obtained:—Alangin A. (M. P. 219°—20°c. with decom.), Alangine B (M. P. 105°—07°c. with decom.) and Alanginine (M. P. 245°—47°c.). They have a tendency to darken in colour in the presence of heat and sunlight. This tendency is maximum in the case of Alangine B and least in the case of Alan-

genine The yields respectively of Alangine A Alangine B and Alanginene on the air dried material are 15% 10% and 001%

Alangine A —(M P 219 —20 C) is a light brown crystalline solid when freshly crystallised from hot benzene but gradually goes on darkening in colour becoming more and more brown under the influence of heat and light It is soluble in chloroform acetone ethylacetate ethyl and methyl alcohols sparingly so in ether benzene, (hot) and insoluble in cold benzene petroleum ether and water It yields marked precipitates with all the alkaloidal reagents and shows colour reactions as given in table 2 below It is soluble in mineral as well as organic acid solution giving in all cases a light orange solution which on evaporation deposits respective salt as an amorphous jelly The salts are extremely bitter in taste and show bluish fluorescence From chloroform solution it deposits at once a dark brown bromine addition product when a solution of bromine in chloroform is added

Found —C =72 26 72 28% N=7 35 7 24% N—8 43 8 25%° (Dumas)

N=4 18 4 24% (Kjeldahl s)

Mol Weight 350 360 (Rast s) 338 6 338 9 (Ignition of the chloroplatinate)

$-OCH_3$—17 49 17 59% Br in bromo compound 40 04 40 23%

$C_{21}H$ O_3N requires —C=71 38 % H=7 08 % N—7 93 %, $=OCH_3$=17 56% (two groups) Br =40 5% (3 bromine atoms), Mol Weight=353

Alangine B M P 105°—07°C It is a deep yellow amorphous solid when freshly obtained It gradually changes to brick red in colour by the action of heat and light and this tendency is greater in this compound than in Alangine A It is easily soluble in chloroform acetone ethyl and methyl alcohols and ethylacetate When freshly prepared it is also easily soluble in ether and benzene but the solubility in these latter solvents goes on decreasing on keeping Probably

that is due to a change of Alangine B to Alangine A. In other properties it is similar to Alangine A.

Found :- C = 72·18; 72·05.%. H = 7·21; 7·13%. N = 8·04. 8·12%. Mol. Wt. = 355; 362 (Rast's). 340·6; 338·9 (ignition of Platinum Chloride.).

$-OCH_3$ = 16·95; 17·13%. Br = 39·85; 40·17%.

$C_{21}H_{19}O_3N$, requires:— C = 71·38%, H = 7·08%, N = 7·93%.

$-OCH_3$ = 17·56%; $C_{21}H_{19}ON$, $\begin{matrix} OCH_3 \\ OCH_3 \end{matrix}$

Br. = 10·5 %, C_2H $Br(Br_2)$ O_3N_2. Mol. Wt. = 353.

Alanginine: -(M.P. 245° -47°C. It is cream coloured amorphous solid. This also changes in colour on keeping but the change is very very slow. It is soluble in ethyl and methyl alcohols, but insoluble in acetone, ethylacetate, benzene and sparingly soluble in ether. The yield of the Alanginine was very small. Its properties and analysis etc., will be given later on when sufficient quantity of it, is isolated in pure form.

Further investigations, regarding structure of the compouds, are in progress.

Table II

—	Frochde's reagent	Erdmanus,	Vanadium chloride.
Alangine A ...	Violet changing to green.	Yellowish brown	Green changing to blue.
Alangine B ..	Ditto	Ditto	Dirty green.

1. Indian Plants and Drugs .. 1908 P. 24.
   By K. M. Nandkarni.
2. Pharmacogorphica Indica .. 1891 Vol. II.
   By W. Dymock.
3. Indegenous group of India .. 1933 P. 272, 273.
   By Lt. Col. R. N. Chopra.
4. Dutt and Sinha . . Indian Academy of Sciences. Vol. XXIII. No. 6. 1946. P. 325.

OXIDATION OF SULPHUR AND ITS COMPOUNDS IN LIGHT

By N R Dhar and B V S Raghavan

Powdered sulphur is largely used in the reclamation of alkali lands in America and Europe 20 to 30 cwts of powdered sulphur are used per acre In his presidential address to the National Academy of Sciences Dhar stated as follows

'In course of time the sulphur added to the soil is oxidized to sulphuric acid by the joint action of bacteria catalysts and light and hence the sodium carbonate of alkali soil is neutralized with the formation of sodium sulphate which can be washed away by flooding the lands From some preliminary experiments N R Dhar and S K Mukherjee[1] concluded that when powdered sulpur is mixed with alkali soil or normal soil more sulphur is oxidized in light than in the dark under identical conditions Purely chemical oxidation of sulphur has been reported to be a slow process and it depended upon the modification of sulphur used In this communication we are submitting the results obtained on the oxidation of finely divided sulphur sodium thiosulphate and sodium sulphide in presence of sand both in sun light and in dark under sterile and unsterile conditions

Experimental (*a*) 100 grs of sand were taken in three sets in Erlenmeyer flasks to each of which 1 gr of powdered sulphur was added To one of the flasks ½ gr of sodium bicarbonate and to a second flask ½ gr of sodium phosphate ($Na_2HPO_4 \cdot 10H_2O$) were added and to the third flask neither carbonate nor phosphate was added Water was added at regular intervals and the flasks were shaken One set of flasks was kept in light and another similar set in dark by covering them with a black cloth The amount of sulphate produced was estimated as barium sulphate making correction for the small amount of sulphate initially present in the flasks before exposure

(*b*) In other experiments instead of powdered sulphur sodium sulphide prepared by passing hydrogen sulphide into solution of

sodium hydroxide, and also sodium thiosulphate were allowed to oxidize in the presence of sand both in light and in dark and under sterile and unsterile conditions The sterilization was carried on in an autoclave at 15 lbs pressure for two hours The results obtained are as follows —

TABLE 1

Surface 100 grs Exposure lasting 100 hrs

Correction was applied for the initial amount of sulphate present

'Unsterile oxidations'

Columns

1	2	3	4	5
Materials used for oxidation		Sulphuric acid obtained with only the oxidisable material + sand	Sulphuric acid obtained with ½ gr $NaHCO_3$ + sand oxidisable material	Sulphuric acid obtained with ½ gr Na_2HPO_4 + sand + oxidisable material
1 gr of sulphur	Light	0 0221 gr	0 0241 gr	0 0251 gr
	Dark	0 0129 gr	0 0155 gr	0 0160 gr
25c c of hypo containing 0 5646 gr of hypo or 0 1613 gr of sulphur	Light	0 0921 gr	0 0964 gr	0 0994 gr
	Dark	0 0678 gr	0 0686 gr	0 0697 gr
25c c of sodium sulphide solution containing 0·1680 gr of sulphur	Light	0 0679 gr	0 0717 gr	0 0766 gr
	Dark	0 0470 gr	0 0481 gr	0 0504 gr

TABLE 2

Surface 100 grs Exposure 3½ months

(Correction was applied for the initial amount of sulphate)

(Sterile and unsterile oxidations)

1	2	3	4	5
Materials used for oxidation		Sulphuric acid obtained with only the oxidisable matter + sand	Sulphuric acid obtained with ½ gr $NaHCO_3$ + sand + oxidisable material	Sulphuric acid obtained with ½ gr Na_2HPO + sand + oxidisable material
1 gr of Sulphur	Light Unsterile	0 1662 gr	0 1997 gr	0 2094 gr
	Light Sterile	0 0881 gr	0 0968 gr	0 1193 gr
	Dark Unsterile	0 0921 gr	0 1176 gr	0 1221 gr
	Dark Sterile	0 0458 gr	0 0613 gr	0 0629 gr
25 c c of hypo containing 0 5654 gr of hypo or 0 1615 gr of sulphur	Light Unsterile	0 3977 gr	0 4115 gr	0 4496 gr
	Light Sterile	0 2236 gr	0 2447 gr	0 2522 gr
	Dark Unsterile	0 3039 gr	0 3118 gr	0 3196 gr
	Dark Sterile	0 1684 gr	0 1804 gr	0 1837 gr
25 c c of sodium sulphide containing 0 1624 gr of sulphur	Light Unsterile	0 2859 gr	0 3033 gr	0 3124 gr
	Light Sterile	0 1643 gr	0 1752 gr	0 1846 gr
	Dark Unsterile	0 1628 gr	0 1684 gr	0 1733 gr
	Dark Sterile	0 0848 gr	0 0902 gr	0 0959 gr

The experimental results show that both under sterile and unsterile conditions more sulphate is formed in the light than in the dark. Moreover in presence of sodium bicarbonate and sodium phosphate there is more of sulphate formation, than in their absence. The longer the time of exposure the greater is the amount of sulphate. These results clearly show that powdered sulphur, sodium sulphide and sodium thiosulphate can be oxidized to sulphate in presence of sand under the complete absence of bacteria; the oxidation is much accelerated by exposure to light in which the amount of oxidation is approximately double that obtained under identical conditions in the dark. Under sterile conditions, like other oxidation processes mild alkali and phosphate accelerate the oxidation of sulphur, sodium sulphide, and sodium thiosulphate both in light and in dark. It is clear therefore that when sulphur or sodium sulphide or sodium thiosulphate is added to the soil or to sand, light, micro organisms and surface facilitate their oxidation to sulphuric acid under tropical conditions.

Summary. These experimental results show that when powdered sulphur, sodium sulphide, sodium thiosulphate are mixed with sand they are slowly oxidized to sodium sulphate. Under sterile conditions the oxidation is less than under unsterile conditions. The oxidation is facilitated by small amounts of sodium bicarbonate and sodium phosphate. Of the three substances investigated sodium thiosulphate seems to be the most photosensitive.

References :—

(1) N. R. DHAR .—Presidential address, Anniversary meeting National Academy of sciences, 1935.

(2) N. R. DHAR & S K. MUKHERJEE. Hill memorial thesis submitted to the Allahabad University, 1937.

(3) WAKSMAN—Principles of soil microbiology pages 527, 1931.

SYNTHESIS OF HIGHER DIBASIC ACIDS FROM LOWER ONES IN THE SERIES

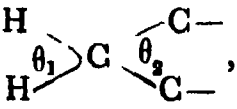
PART I

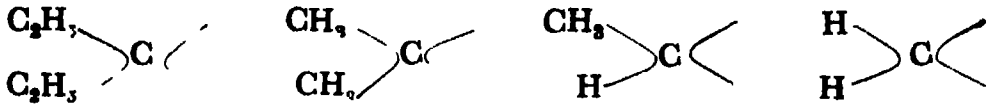
Synthesis of ββ-dimethyl and ββ-diethyl-adipic acids

By

L. D. TEWARI AND J. D TIWARI

van't Hoff in his structural theory did not postulate the carbon tetrahedron to be rigid and the directions of the valencies were what he said, only when the four groups attached to them were identical and were hydrogen atoms. (Sidgewick, 'Covalent links' page 201). A change in the directions of the valencies occurred by loading them with uneven molecules. The tetrahedral angle of Baeyer $2 \tan^{-1}\sqrt{2} = 109{\cdot}5°$, was the angle subtended at the centre by one of the sides. The change in the angle produced by substituents was calculated by Thorpe and Ingold on the basis of the molecular volume of the attached groups, Traube's[1] constants for the atomic volumes of methyl and carbon atoms were made use of, in determining these values.

When four hydrogen atoms were attached to the carbon atom the normal angle was 109°28′. This changed with the different load on the valencies. In  , θ_2 is greater than θ_1, because molecular volume of carbon is greater than that of hydrogen. Any attempt to reduce θ_2, which can be done by changing θ_1, will lead to easier formation of a carbon ring, if the arms which subtend the angle were open chains. Thorpe and Ingold have furnished experimental evidence to prove that the ease of cyclopropane ring formation was in the following order. It decreased from (i) to (iv) and was least in the case of (iv).

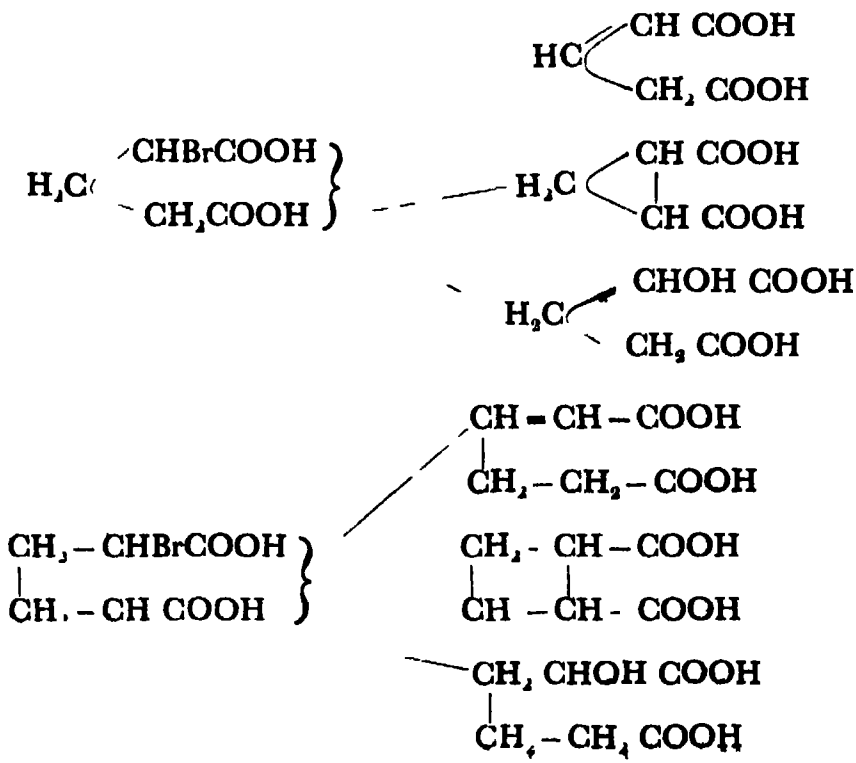


(I) (II) (III) (IV)

This is a chemical evidence on which the 'Deflexion Hypothesis' is based. The experimental value of β alkyl substituted glutaric acids are in agreement with the above.

β alkyl substituted glutaric acids facilitate the formation of a three membered ring system If in one of the arm chains attached to β-carbon atom in alkyl substituted glutaric acids, one more methylene group be introduced, it should facilitate the formation of a cyclobutane ring, under the conditions where β alkyl substituted glutaric acid yielded a cyclopropane ring

Thus in α haloginated glutaric and α dipic acids the action of alkali can be postulated as follows·



Actual experiments of Ingold and other show that with dilute alkali nearly whole of the acid is converted into hydroxy acid and with concentrated alkali about 50% of cyclopropane derivative was produced contaminated with hydroxy acid and a trace of glutaconic acid, when glutaric acid was examined In case of adipic acid, a marked difference was observed Ethyl α chloroadipate, and ethyl α bromoadipate on boiling with 2N sodium carbonate yielded 90% hydroxy adipic acid The above halogen compounds of adipic acids under exactly similar conditions as have been used in cases of similar glutaric acid compounds, on treatment with strong alcoholic (methyl) potash, gave cyclobutane dicarboxylic acid only in traces and the greater portion of the identified material was hydroxy product The experimental evidence indicated that the formation of cycolbutane ring is attended with considerable difficulty as compared to the formation of cyclopropane ring, even when the similar methods were used for their preparation The cyclopropane ring formation in the alkyl substituted glutaric acids was in the order predicted by Thorpe and Ingold's hypothesis

Spiers and Thorpe were convinced that the introduction of gem groups into malonic acid or into glutaric acid in ββ position leaves the symmetry of the molecule unchanged There is thus no free rotation effect to be considered and acids of such series are strictly comparable with one another In succinic acid although the symmetry of the molecule is modified slightly yet the same applies to it

It remained to be determined how similarly substituted adipic acids behaved The field had remained unexplored for the synthesis of such adipic acids was attended with considerable difficulties

The usual methods for the conversion of a lower dibasic acid into a higher one fail when applied for the preparations of substituted adipic acids Then it was proposed, that attemps to introduce a methylene group in one of the free arm chains carrying carboxyl groups in glutaric acids (ββ-substituted), be made A method was devised on the lines, based on the conversion of ortho-nitro-benzoic acid into, ortho-

nitro-phenyl-acetamide[4], and experiments were started to convert ββ-dimethyl and ββ-diethyl-glutaric acids into corresponding adipic acids ββ-dimethyl and ββ-diethyl glutaric acids were prepared from acetone, diethyl ketone and cyanaceticester in ice cold alcoholic ammonia The imide formed was hydrolysed with strong sulphuric acid, and ββ-dimethyl glutaric acid was purified and converted into anhydride The anhydride was boiled with absolute alcohol and ethylhydrogen ββ-dimethyl glutarate formed was treated with thionyl chloride The chloride formed by the replacement of the free hydroxyl group in the acid ester, was allowed to interact with diazomethane The diazo-ketone was turned into the amide of ββ-dimethyl-adipic acid by the action of ammonia and silver nitrate on its alcoholic solution On hydrolysis the amide yielded the corresponding valerolactone instead of the desired acid and ββ-diethyl glutaric acid yielded a mixture of the valerolactone and ββ-diethyl adipic acid The tendency of β substituted amide seems to form a six membered lactone ring in preference to acid and hence frothing during hydrolysis showing evolution of carbondioxide From further experiments it is evident that this tendency decreases with increase in volume or complexity of the β-substituted group The amide of dimethyl acid is under further investigation The valero-lactones were converted into corresponding acids by Blanc's method[4] Details of the preparations will be found in the experimental part In Blanc's process the preparation of lactone is not easy, consequently the starting material is not easily accessible and the process becomes increasingly difficult for other β-substituted acids which however have been synthesised by the authors method In adipic acid the β-carbon atom from one Carboxyl group is γ-from another All the alkyl substituted adipic acids synthesised are named as ββ-derivatives

Further work in connection of synthesis of other adipic acids and their bearing as a whole on the 'Valency deflection hypothesis' is in progress

EXPERIMENTAL

Ethyl Hydrogen ββ-Dimethylglutrate

60 gms ββ-dymethyl glutaric acid was prepared by Thole and Thorpe's method[3] and was converted into its anhydride

50 gms ββ-dimethyl glutaric anhydride was converted into ethyl hydrogen ββ-dimethyl glutrate and then into its chloride by interaction with thionyl chloride

Two instalments of 14 4 gms each of the chloride, were worked up for the preparation of ββ-dimethyl adipic acid

Reaction with Diazomethane

14 4 gms of chloride were dissolved in 50 c c pure dry ether and the solution was added to a solution of diazomethane (3 gms) in ether (300 c c cooled to −20°C) The gradual addition of the former to the latter took about 45 minutes The evolution of gas began to take place from the reaction mixture when the temperature rose to −14°C The mixture was kept over night and the next day the ether and excess of diazomethane were removed at the pump The temperature reached by it the previous night was 20°C The residue obtained after the removal of the solvent was treated with ammonia solution as follows

ββ-Dimethyl Adipic Acid

3 4 gms ammonia gas was dissolved in 300 c c alcohol at 0°C and the above residue dissolved in 50 c c alcohol was added to it 7 5 c c 10% aqueous silver nitrate was also added and the reaction mixture was left to stand over night Next day it was diluted with 50 c c alcohol and heated on a water bath Gas evolution was noticed at 50°C During four hours heating the temperature of the reaction mixture was raised upto 70°C It was then filtered hot and diluted with water The precipitated amide was digested *in situ* with 10% caustic potash and refluxed for six hours The alkaline solution was allowed to cool Then it was acidified with 2 normal sulphuric acid saturated with ammonium sulphate and extracted several times

with ether. The combined ethereal extract on being washed, dried with sodium sulphate and evaporated to dryness yielded a lactone, which was identified as ββ-dimethyl-valero-lactone. It had a M.P. 29° – 30° and a B.P. 234° – 235°.

Small quantities of the lactone (2 gms. each) were sealed with potassium cynide in glass tubes and the tubes were strongly heated. They were then allowed to cool and were cautiously opened and the contents treated with sulphuric acid. The acidic solutions were combined and saturated with ammonium sulphate. The acidic solution was extracted with ethers everal times, the ethereal solution dried with sodium sulphate, and evaporated to dryness.

ββ-dimethyl-adipic acid thus obtained was found to contain C = 55·04 % and H = 8.0 %. $C_8H_{14}O_4$ requires C = 55.17 %, H = 8.05%. M.P. 87°.

ETHYL-HYDROGEN—ββ-DIETHYL GLUTARATE.

60 gms. ββ-diethyl glutaric acid prepared by. Deshpande and Thorpe's method[7], were heated under reflux with 50 c.c. acetyl chloride for three hours.Acetyl chloride was removed under reduced pressure and the residue was extracted with dry ether. The anhydride was obtained by the removal of the solvent from the ethereal extract.

50 gms. ββ-diethyl glutaric anhydride was converted into ethyl hydrogen-ββ-diethyl glutarate, using 18c.c. absolute alcohol and heating it under reflux. The method followed for this conversion was Qudrat-i-Khuda's method[8].

CONVERSION INTO CHLORIDE

The acid ester (36 gm.) was converted into chloride by interaction with thionyl chloride (30 c.c.)[9].

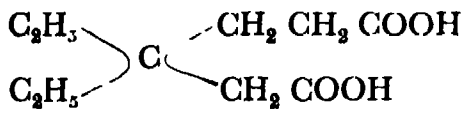
The chloride distilled under reduced pressure of 15—20 m.m. at 140° – 145°C. Yield 32 gms.

It was treated with diazomethane in two successive batches 16 gms. each and then converted into amide from which the acid was obtained on hydrolysis.

Reaction with Diazomethane

A solution of diazomethane (gms.)in ether (300 c.c.) was cooled to −20°C and 16 gms. of freshly distilled chloride obtained as stated above dissolved in 50 c.c. of pure dry ether were added in drops with continual shaking to it and the addition was completed in 45 minutes. The temperature of the reaction mixture was then allowed to rise slowly. Gas evolution from it started when the temperature reached − 12.5°C. The temperature of the reaction mixture was maintained at −12·5°C to −10°C till the gas evolution ceased It took about two hours. The reaction mixture was kept over night and the maximum temperature reached by it till it was subjected to further treatment was 20 C The solution indicated that some unreacted diazomethane was present in it and that an excess of the reagent was used. Excess of diazomethane and ether were removed at a reduced pressure and the residue obtained from two such operations was subjected to further treatment in two separate batches, till the required acid was obtained

ββ Diethyl Adipic acid



3.5 gms. ammonia gas was dissolved in 100 c.c. absolute alcohol at 0°C. The residue obtained from the above reaction was dissolved in 50 c.c. alcohol and mixed with ammonia solution. 7.5 c.c. of 10% silver nitrate was also added and the whole was allowed to stand over night, when it reached a maximum temperature of 18°C. It was then heated on a water bath after diluting it with 50 c.c. alcohol. The maximum temperature attained by the water bath was 70°C, as the heating was always so regulated that no vigorous evolution of gas from the solution may take place. At the end of four hours, the reaction mixture was filtered hot and diluted with water. The precipitated amide was digested with 10% caustic potash and was heated under reflux for six hours. It was allowed to cool and then acidified with 2 normal sulphuric acid. The acidified solution was saturated

with ammonium sulphate and extracted several times with ether. The ethereal extract was dried over sodium sulphate and the solvent was removed. This ethereal extract yielded a liquid residue, yellow in colour. The residue was distilled under reduced pressure and a light yellowish oil was obtained from it at 18°/42 m.m. When this oil was removed from the pump and the liquid was naturally subjected to normal pressure and room temperature, white needles separated from it. It was kept in a dessicator over calcium chloride, so that the separation of the crystalline matter may reach completion. After two days the crystalline substance was separated from the oily mother liquor, washed with a little ether, dried by pressing it between filter papers, recrystallised from ether, and examined. It was found to be ββ-diethyl adipic acid and melted at 133° -134°C. It yielded a silver salt with silver content 52.0% and $C_{10}H_{18}O_4Ag_2$ requires Ag = 51.92%. It contained C = 59.31% , H = 9.0%; $C_{10}H_{18}O_4$ requires C = 59.41%, H = 8.91%.

The liquid which remained after the removal of the acid was found to be lactone. B.P. 136° 138 /20 – 22 m.m.

References

1. Traub, J. 1920, **117**, 1579.
2. Spiers and Thorpe, J. 1925, **127**, 538.
3. Arndt and Eistert, Ber., 1935, 6, 204
4. Gustave Blanc Compt. Rend, 1904, **139**, 800—802.
5. Thole and Thorpe J , 1911, 434.
6. Muhommad Qudrat-i-Khuda J., 1929, 208.
7. Deshpande and Thorpe J , 1922, 435.
8. M. Qudrat-i-Khuda J , 1929, 1919.

SYNTHESIS OF HIGHER DIBASIC ACIDS FROM LOWER ONES IN THE SERIES

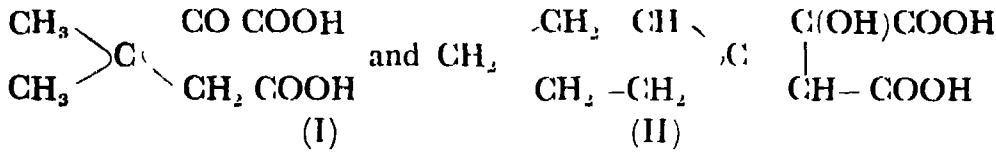
PART II

SYNTHESIS OF CYCLOHEXANE-1-ACETIC-1-PROPIONIC AND CYCLOPENTANE-1-ACETIC -PROPIONIC ACIDS

By L. D. Tewari and J. D. Tiwari

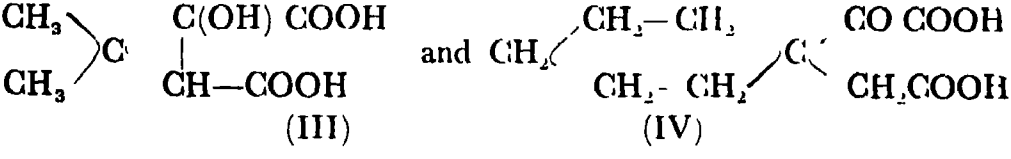
Experimental data of Thorpe, Ingold and many of their co-workers showed that when the two valencies of β-carbon atom in glutaric acid are included in a ring complex and cyclopentane residue occupied this position, then it was found to behave as a strainless ring i.e., cyclopentane behaved just like a gem dimethyl group. Cyclohexane ring in a similar position behaved as a strained ring.

Examination of β-substituted glutaric acids convinced Thorpe and his co-workers that a comparatively small alteration in the angle, particularly as regards the stability of the open chain and ring system was attended with a marked difference in chemical behaviour of the compound. Thus the acids



(I) (II)

are the stable forms though the acids



(III) (IV)

are capable of existence and it has been found possible to prepare them. It is evident that $(CH_3)_2$: group and cyclohexane residue favour the formation of acids (I) and (II) and not of the acids (III) and (IV) respectively.

It remained to be determined how similarly substituted adipic acids behaved Experiments were started to convert cyclohexane and cyclopentane 1 1 diacetic acids into cyclohexane and cyclopentane 1 acetic 1 propionic acids by the method devised in Part I of this series

Cyclohexane 1 1 diacetic acid was prepared by the general method of Guareschis by the treatment of a mixture of cyano acetic ester and cyclohexanone with alcohol saturated with ammonia in freezing mixture at 0 The acid formed was hydrolysed with strong sulphuric acid and cyclohexane 1 1 diacetic acid obtained was purified and converted into anhydride The anhydride was boiled with absolute alcohol and ethyl hydrogen cyclohexane 1 1-diacetate formed was treated with thionyl chloride The chloride formed by the replacement of the free hydroxyl group in the acid ester was allowed to interact with diazomethane The diazo ketone was turned into the amide of cyclohexane 1 acetic 1 propionic acid by the action of ammonia and silver nitrate on its alcoholic solution The amide on hydrolysis with sulphuric acid yielded cyclohexane 1 acetic 1 propionic acid Cyclopentane 1 acetic 1 propionic acid was also prepared by applying the above method using the corresponding cyclopentane compounds

EXPERIMENTAL

ETHYL HYDROGEN CYCLOHEXANE 1 1 DIACETATE

100 gms cyclohexane 1 1 diacetic acid prepared by Thole and Thorpe's method were heated under reflux for three hours with 80 c c acetyl chloride The acetyl chloride was removed completely at the pump under reduced pressure and the remaining residue was repeatedly extracted with dry ether The anhydride of cyclohexane 1 1 diacetic acid was obtained by removing the solvent from the ethereal solution

80 gms of cyclohexane 1 1 diacetic anhydride prepared as above were refluxed with 60 c c of absolute alcohol for five hours A calcium chloride guard tube was attached to the open end of the reflux condenser Excess of alcohol was removed after the refluxing was over,

at a temperature 50°-55° of water bath, under reduced pressure. The thick syrupy residue left in the distilling flask was mixed with 200 c.c. water to dilute the alcohol, if any, had remained in the ester residue. The crude ester which separated at this stage as an oily liquid was removed from the aqueous layer with the help of a separator, after taking it up in ether. The aqueous portion was extracted with ether a few times more to ensure complete removal of ester from it. The ethereal extracts were combined and then extracted several times with a solution of sodium carbonate The combined sodium carbonate extracts on acidification with dilute hydrochloric acid liberated an oil of syrupy consistency and was ethyl-hydrogen-cyclohexane-1 : 1-diacetate. It was dissolved in ether and the ethereal solution was dried over sodium sulphate The dried ethereal solution on removal of the solvent yielded pure dry ethyl-hydrogen-cyclohexane-1 : 1-diacetate. It showed a marked tendency to decompose on exposure. A freshly prepared sample when converted into silver salt and examined for its silver content gave a quite satisfactory value. (Obtained value Ag. = 32.40%, $C_{12}H_{17}O_4Ag$ requires Ag ≡ 32.24 %).

The acid ester distilled at 188°-190°C under a diminished pressure 3-5 m.m., but the distillate was found to have undergone a considerable amount of decomposition. It appears that it is impossible to distill the acid ester even under reduced pressure, without undergoing some decomposition.

Conversion of acid ester into chloride

50 gms. freshly prepared ethyl-hydrogen-1 : 1-diacetate was mixed with 40 c.c. freshly distilled thionyl chloride slowly, with shaking, and the mixture was refluxed for three hours in a water bath, raising the temperature of water in the bath gradually upto 80°C. The reaction was allowed to complete by keeping the reaction mixture at a temperature of 80°C for about an hour. After this period, unreacted thionyl chloride was removed under reduced pressure and the residue was vacuum distilled. The chloride was obtained as a colourless mobile liquid (yield 44 gms.) B.P. 166°-168° at 4-6 m.m. pressure.

REACTION BETWEEN THE CHLORIDE AND DIAZOMETHANE

A solution of diazomethane in 200 c.c. pure dry ether at -20°C, was obtained from nitroso-β-methyl amino-isobutyl methyl ketone and ten per cent caustic alcoholic potash. It represented 2.5 gm diazomethane gas and this quantity of diazomethane was decidedly more than required for the reaction.

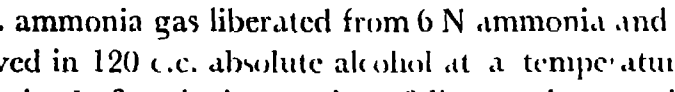
In one of the holes of a double bored thoroughly waxed cork, which exactly fitted the neck of the flask containing diazomethane solution, to form an air tight joint, a dropping funnel was inserted. Through the other bore passed a delivery tube bent twice at right angle in the same direction The longer arm of the tube was fitted in another double bored cork, the other bore of which carried an exit tube. This cork was fitted to a second flask containing about 50 c.c. ether. A calcium chloride guard tube was fitted to the dropping funnel in the first flask, by removing its stopper The whole arrangement was so made as to exclude any moisture from coming into contact with the reacting materials.

10 gms. freshly distilled chloride was dissolved in 50 c.c. pure dry ether and put in the dropping funnel, fitted to the flask containing diazomethane solution at -20°C in ether. The solution of the chloride was then slowly run in, drop by drop in the diazomethane solution with continual shaking. This operation took about half an hour. The speed of addition was so regulated as not to change the temperature of the diazomethane solution appreciably. After the addition was over, the mixture was shaken thoroughly and the temperature maintained at -20° for another half an hour. It was then allowed to rise slowly. At -8°C, gas evolution was observed to occur in the solution. The gas evolution of the reaction mixture was allowed to complete at a temperature -8°C to -5°C. The reaction mixture was then left to stand over night, and the maximum temperature attained by it during that period was 18°. At the end of this time the colour of diazomethane still persisted, as decided excess of the reagent was used. The ether and excess of diazomethane were removed at the pump and the

residue was stored at a diminished pressure. 40 gms. chloride was converted into the diazo-compound in small batches of 10 gm. each and the combined residue was used for further reaction, in two instalments.

2

CYCLOHEXANE-1-ACETIC-1-PROPIONIC ACID



4 gms. ammonia gas liberated from 6 N ammonia and caustic Soda, was dissolved in 120 c.c. absolute alcohol at a temperature 0°C. The residue obtained after the interaction of diazomethane and the chloride (20 gm.) was dissolved in 60 c.c. alcohol mixed with above ammonia solution. 8 c.c. of 10 % silver nitrate solution was then added and the reaction mixture was allowed to stand over night. Next day 60 c.c. ordinary alcohol was added to the solution to decrease the concentration of ammonia, and the solution was then warmed on a water bath. The heating was continued and the reaction was never allowed to become vigorous. The maximum temperature reached at the end of four hours was 70°C. Then the gas evolution from the solution ceased. The reaction mixture was filtered hot. The filtrate on dilution with water deposited the amide in a very fine form and it settled down very slowly. It was hydrolysed with 10 % caustic postash by heating it under reflux with alkali for five hours. The alkaline hydrolysis mixture was cooled and acidified with 2 normal sulphuric acid. The acidified solution was saturated with ammonium sulphate and repeatedly extracted with ether. The ethereal extracts were combined, dried with sodium sulphate and the solvent ether removed. A slightly sticky brownish solid mass was thus obtained. It was washed with small quantities of chloroform, which dissolved the coloured substance and a little of the solid as well. The chloroform extract on evaporation left a liquid residue. The white solid left after chloroform treatment was washed with petrol ether in which it was insoluble and was crystallised from benzene. It was very soluble in ether and

dissolved in hot water, and was cyclohexane-1-acetic-1-propionic acid. M.P. 169°C. It forms a silver salt which explodes on heating. (Obtained Ag = 50.45 %, $C_{11}H_{1}O_{4}Ag_{2}$ requires Ag = 50.47 %. On combustion the compound gave the value, C = 61.62 %, H = 8.39 %: $C_{11}H_{18}O_{4}$ requires C = 61.68%, H = 8.41 %.

3

ETHYL-HYDROZEN-CYCLOPENTANE DIACETATE

60 gms. cyclopentane-1 : 1-diacetic acid prepared by Norris and 3 Thorpe's method, was converted into its anhyride by heating it under reflux for three hours with 50 c.c. acetyl chloride. After the removal of acetyl chloride the residue was extracted with dry ether and the ethereal extract on removal of the solvent yielded the anhydride of cyclopentane-1: 1-diacetic acid.

50 gms. cyclopentane-1 : 1-diacetic anhydride was dissolved in 36 c.c. absolute alcohol and heated under reflux for six hours on a steam bath. 100 c.c. water was added to the residue and the precipitated oil was taken up in ether. The ethereal solution was extracted repeatedly with sodium carbonate. The alkaline extracts were combined and acidified with dilute hydrochloric acid, when the acid ester separated as an oil. It was treated with ether in which it dissolved and thus extracted from the acidified solution. The acidified solution was shaken with ether three times and combined ethereal extract was dried with sodium sulphate after washing it free from acid. The ether was then removed and the residue which was the acid ester of cyclopentane-1:1-acetic acid was tested for its purity by converting it into silver salt and determining the silver content (Ag = 40.94 %, $C_{11}H_{17}O_{4}Ag$ requires Ag = 41.12 %). It distills with decomposition at 180°-182°/3-5 m.m.

CONVERSION OF ACID ESTER INTO CHLORIDE

32 gms. ethyl-hydrogen-cyclopentane-1 : 1-diacetate was treated with 28 c.c. thionyl chloride and was refluxed for three hours, heating it on a water bath. The temperature of water in the bath was raised slowly to a maximum of 80°C towards the end. After the refluxing

was over the excess of thionyl chloride was removed under reduced pressure and the residue vacuum distilled The chloride distilled at 125° 128°/4 9 mm yield 33 0 gms Two instalment of 16 gm each were treated with diazomethane and subjected to further reactions

Reaction with Diazomethane

A solution of 3 gms diazomethane in 300 c c pure dry ether was cooled to 20 C and a solution of 16 gms chloride prepared as above in 50 c c pure dry ether was slowly added during 45 minutes with continual shaking of the reaction mixture The temperature was allowed to rise after the addition was over When the temperature reached 15 C gas evolution from the reaction mixture was observed and this was allowed to complete between 12 C and 15 C by carefully manipulating the temperature It was then left over night and the maximum temperature reached by the reaction mixture during that period was 18 C. The colour of diazomethane still persisted Ether was removed at the pump and the residue converted into amide as follows

Cyclopentane 1 acetic 1 Propionic acid

$$\begin{matrix} CH_2—CH_2 \\ CH_2—CH_2 \end{matrix} C\begin{matrix} \diagup CH\ COOH \\ \diagdown CH\ CH\ COOH \end{matrix}$$

3.5 gms ammonia gas was dissolved in 100 c c absolute alcohol at 0°C. The residue obtained from the previous experiment was dissolved in 50 c c. alcohol and was added to the solution of ammonia 7.5 c.c. of 10 % silver nitrate was also added and the whole was allowed to stand over night. Next day it was diluted with 50 c c alcohol and carefully heated on a water bath Gas evolution was noticed at 50 C The temperature of the bath was raised upto 70 C during three hours heating This reaction mixture was filtered hot and then diluted with water when the amide was precipitated as a fine powder. This amide was hydrolysed by refluxing it with 10 % caustic potash for six hours The alkaline solution was cooled

acidified with 2 normal sulphuric acid, saturated with ammonium sulphate and extracted several times with ether The ethereal extracts were combined and the solvent was removed after the extract had been washed and dried over sodium sulphate. The residue, which was semi-solid and stricky was washed with chloroform. After the chloroform washing, the solid which was left, was crystallised from ether, when it was obtained as a white crystalline substance melting at 173 C. This was cyclo-pentane 1-acetic, -1-propionic acid. It formed a silver salt. (Ag 52.0 % obtained, $C_{10}H_1O4$-Ag requires Ag = 52.12 %). It contained C 59.96 %, H 8.1 % C_1H_1O4 requires C = 60.0 % H = 8.0 %.

Chemistry Department.
Allahabad University.

N B —There is difference between the melting points, the acid prepared by Norris melts at 142° and the same acid prepared by the authors by different method melts at 169° Impurity may be the cause the analysis of the amide which was not separated by the authors but hydrolysed in situ is now under investigation and the authors are now preparing the acid by Norris method also, and a comparision of the two samples prepared by different methods will reveal their identity or otherwise

(1) Thole and Thorpe. J. 1911, 440.
(2) Norris. J. 1926, 250.
(3) Norris and Thorpe. J. 1921, 1208

COMPARATIVE EXPERIMENTS WITH INORGANIC AND ORGANIC MANURES REGARDING THE NITROGEN POSITION OF THE SOILS.

PART I

N. R. DHAR AND B. G CHATTERJEE

SUMMARY

1 Cowdung (farmyard manure) neem leaf (Melia azadirachta Linn) and other carbonaceous substances when added to the soil fix nitrogen of the air and improve the nitrogen status whilst with ammonium sulphate the nitrogen status remains stationary By adding two doses of these carbonaceous substances the nitrogen content of a soil in Allahabad was raised from 0 038 to 0 09 % with wet cowdung at the rate of 68 tons per acre with neem leaf at the rate of 30 tons per acre it went up to 0 0815 % whilst with ammonium sulphate even at the rate of 742 lbs of nitrogen per acre there was no increase of total nitrogen after three months Even with 1484 lbs per acre the nitrogen status was not improved

2 These results obtained in India are in agreement with those obtained in the classical experiments at Rothamsted

On the application of farmyard manure in Rothamsted fields for a number of years the soil nitrogen which was originally 0.122% rose to 0.256% from 1842 to 1914 whilst the soil without any manure fell to 0.095% With complete artificials the status of nitrogen was 0.099%. Russell[1] has reported that the yield of barley and straw with farmyard manure in the Rothamsted field experiments was better than that obtained with complete artificial manures. The following data[2] from the Rothamsted fields present a clear picture of the nitrogen position of some of the plots —

Total nitrogen balance sheet (1865 1914) in top nine inches of soil,

	Farmyard manure.	No manure	Complete Plot 7	Artificials Plot 13
Total nitrogen in soil in 1865 in lbs. per acre.	4850	2960	3390	3320
Total nitrogen in soil in 1865 per cent.	0.196	0.114	0.123	0.121
Total nitrogen in soil in 1914 in lbs. per acre.	5590	2570	3210	3240
Total nitrogen in soil in 1914 in per cent	0.236	0.092	0.120	0.122
Total change in 49 years in lbs. per acre.	+740	−390	−180	−80

In order to find out whether these results are reproducible under Indian conditions, experiments have been taken up at Allahabad in the laboratory and under field conditions. Ammonium sulphate, freshly plucked neem leaves (Melia azadirachta Linn), fresh cowdung, oil cake and straw were added to the soil in different concentrations and the doses were repeated when the carbon/nitrogen ratio of the soil treated previously with manures attained the value of 10:1.

Experimental.

1. 250 grms. of soil were placed in 6 dishes and 6 pyrex glass flasks. About 40, 20, and 10 grms. of cowdung were added to various dishes and flasks and thoroughly mixed. The original C and N contents of these mixtures were estimated by the modified Kjeldahl method[3]. For experiments under sterile conditions the flasks were sterilised in an autoclave at 15 lbs. pressure for 30 minutes and the sets were then placed in light and in the dark by covering them with black cloth.

2. Similar experiments were carried on with different concentrations of neem leaves. The doses added were 15 grms., 8 grms., and 3.5 grms. to 250 grms. of soil.

with neem leaf was 32 millions and 122 millions, though the efficiency in both the cases was approximately double in light than in dark. The following medium was used for Azotobacter counts:—

Tap water	...	1 litre.
Mannite	...	20 grms.
K_2HPO_4	...	0.2 grm.
Agar	...	20 grms.

Sanai (Crotalaria Juncea—recommended as an excellent manure by the agricultural department)' and wheat straw were also tried in dishes mixed with soil. They are oxidised very slowly The efficiency with wheat straw is 24 in light and 11.2 in the dark, whilst the efficiency in case of sanai is low, 5.7 in light and 3.3 in dark.

Ammonium sulphate when added to the soil gets completely lost in three months mostly as nitrogen gas during the formation and decomposition of the unstable substance ammonium nitrite". Carbonaceous matter apart from nitrogen fixation acts as a protector of nitrogen when added with artificial manures. 10 grms. of cowdung in 150 grms. of soil reduced the loss of 0.06% of added ammonium sulphate nitrogen from 69.16% to 44·3% in one month.

A typical table showing the fixation of nitrogen by the oxidation of cowdung.

First application of cowdung in the field.
56Kg. of cowdung in plot 4′ × 4′ ≡ 136 tons. per acre.

Date		Total –C.%	Total –N%.	Efficiency
		EXPOSED		
23-5-'47	...	1.446	0.0920	...
25-6-'47	...	1.304	0.0941	15.0
		COVERED		
23-5-'47	...	1.452	0.0928	...
25-6-'47	..	1.372	0.0934	7.5

28 Kg. of cowdung in plot of 4′ × 4′ = 68 tons. per acre.

EXPOSED

Date		Total C%	Total –N%	Efficiency
24-5-'47	...	0.932	0.0652	
26-6-'47	...	0.801	0.0673	16.2

COVERED

Date		Total C%	Total –N%	Efficiency
24-5-'47	...	0.946	0.0678	...
26-6-'47	...	0 871	0.0681	8.0

Second application of cowdung in the field.

56 Kg. of cowdung in 4′ × 4′ plot = 136 tons per acre.

EXPOSED

Date		Total C%	Total N%	Efficiency
15-11-'47	...	2.088	0.1458	...
10-3-'48	..	1.596	0.1517	12.0

COVERED

15-11-'47	...	2.146	0.1476	...
10-3-'48	...	1.865	0.1496	7.1

28 Kg. of cowdung in 4′ × 4′ plot = 78 tons per acre.

EXPOSED

Date		Total C%	Total—N%	Efficiency
15-11-'47	...	1.1214	0.0856	...
10-3-'48	...	0 893	0.0901	14.1

COVERED

15-11-'47	...	1.249	0.0942	...
10-3-'48	...	1.064	0.0956	7.5

A typical table showing the fixation of nitrogen by the oxidation of neem leaves

12 Kg. of neem leaves in 4′ × 4′ plot = 36 tons per acre,

100 grms of soil (C% – 0 386, N% – 0 0386) + 0 2828 grm of ammonium sulphate (0 06% nitrogen)

Condition	Hours Of exposure	Date	Total — C%	Total— N%	% Loss
Exposed	0	16 8 '47	0 386	0 0986	
Covered			0 386	0 0986	
Exposed	200	18-9-'47	0 384	0 0571	69 16
Covered			0 386	0 0709	46 16
Exposed	600	27-11- 47	0 384	0 0384	100 0
Covered			0 384	0 0386	100 0

100 grms soil + 0 1414 grm of ammonium sulphate (0 03% nitrogen)

Exposed	0	16-8-'47	0 386	0 0686	
Covered			0 386	0 0686	
Exposed	200	18-9-'47	0 384	0 0434	84 00
Covered			0 384	0 0507	59 67
Exposed	600	27-11-'47	0 384	0 0384	100 00
Covered			0 384	0 0390	98 70

The forgoing results show conclusively that repeated application of cowdung and neem leaf enrich the soil markedly by increasing the nitrogen by fixation as well as retaining the added nitrogen whilst ammonium sulphate does not improve the soil nitrogen position These results are in agreement with those obtained in Rothamsted

Chemical Laboratories,
Allahabad University

REFERENCES

1 Russell . 'Soil conditions and plant growth' Ed 1932, pp. 78

2. Russell 'Soil conditions and plant growth' Ed 1932, pp 361

3 Robinson, McLean & Williams J Agric Sci 1929, **19**, 315

4. Dhar and Mukerji ... Proc. Acad. Sci. U. P. 1934, **4**, 175.
1935, **9**, 330; 1935, **5**, 61.

5. Clarke ... Presidential address-Science congress Allahabad—1930.

6. Dhar ... Proc. K. Akad. Wetensk. Amsterdam. **23**, 308, 1920.

Nature, 1934, **134**, 572.

LOSS OF NITROGEN IN BACTERIAL NITRIFICATION OF NITROGENOUS MANURES

PART I

N. R. Dhar and M. C. Pant

Russell[1] has stated that "The essential facts of nitrification are readily demonstrated by putting a small quantity of soil—0·2 to 0·5 gm. into 50 c.c. of a dilute solution of ammonium sulphate containing nutrient inorganic salts and some calcium or magnesium carbonate but no other carbon compound. After three or four weeks at 25° the ammonia is all gone and its place is taken up by nitrates. The conversion is almost quantitative, only an insignificant quantity of nitrogen being retained by the organism."

In several publications since 1934, Dhar[2–6] and coworkers have recorded marked loss of nitrogen during nitrification of organic and inorganic nitrogenous manures. Similarly the experiments carried on in Rothamsted[7] fields show that when about 100 lbs. of nitrogen per acre as ammonium sulphate are added about 65% are lost without benefit to the soil or crop. We have explained this loss on the view point that in the process of nitrification in nature the unstable substance ammonium nitrite is formed and this decomposes[8] readily into nitrogen gas and water. Moreover we have emphasized that the amount of nitrate produced in a soil on the addition of a nitrogenous manure need not be the measure of the amount nitrified, as the loss of nitrogen in the gaseous state usually exceeds the amount of nitrate obtained in nitrification.

In order to test whether a similar loss of nitrogen during the bacterial nitrification of nitrogenous manures takes place we have undertaken a systematic research on this line.

EXPERIMFNTAL —

The following culture medium was prepared for the growth of nitrifying bacteria and the nitrification to take place

Potassium phosphate	(K_2HPO_4)	1 0 gram
Sodium chloride	(NaCl)	2 0 grams
Ferrous sulphate	($FeSO_4$)	0 1 gram
Distilled water		1000 c c
Magnesium carbonate	($MgCO_3$)	Excess (0 5 gm per 100 c c)

50 c c of this culture solution was placed in 300 c c conical flasks (Pyrex) after thoroughly shaking it The flasks were plugged with absorbent cotton wool and were sterilized in an autoclave at 15 lbs pressure for 30 minutes A 10 % solution of ammonium sulphate was prepared and sterilized separately From 1 c c to 10 c c of this ammonium sulphate solution was added to various flasks with the culture solution by a sterilized pipette 1 gram fresh garden soil was inoculated in each flask The flasks were then incubated at 30 (±0 5°) for a period of 7 weeks and then analysis was made by the following method

The solution after incubation was leached with potassium chloride water (5%) and after filteration was made upto 200 c c The ammoniacal nitrogen left was estimated by developing colour with Nessler s reagent and comparing with a standard solution (0 0004% nitrogen) of ammonium sulphate by a Duboscq colorimeter

50 c c portion of the leached solution was taken in a flask and distilled with dilute solution of caustic soda (1%) The ammonia liberated was trapped in dilute sulphuric acid and was estimated colorimetrically Now to this distilled solution was added Devarda s alloy (2 0grams) and 25 c c of 1% caustic soda solution and the flask was well corked and kept overnight The nitric nitrogen was reduced to ammonia This was again distilled next day and nitrogen was estimated as above Thus the ammoniacal and nitric nitrogen were estimated The following results were obtained —

TABLE—I With ammonium sulphate

S. N.	Original Soln. in c.c	N content N gram	NH_3–N left	NO_3–N formed	Total N left	Total N loss	Loss
1	10·0	0·2121	0 1[illegible]2	0 0178	0 1506	0 061[illegible]	28 9
2	7 0	0 1185	0 0776	0 0160	0 0936	0 0549	37 1
3	5 0	0 1061	0 0289	0 0152	0 0441	0 0620	58 1
4	2 0	0 0424	0 0031	0 0118	0 0149	0 0275	64 6
5	1·5	0 0318	0 0019	0 0080	0 0099	0 0219	68 5
6	1 3	0 0275	0 0008	0 0041	0 0049	0 0226	81 8
7	1·0	0 0210	0 000[illegible]	0 00 4	0 0039	0 0171	82 0

Similar experiments were performed with ammonium persulphate and ammonium phosphate solutions as source of ammoniacal nitrogen and the following results were obtained after analysis

TABLE II With ammonium persulphate

S N	Original Soln. in c c	N content N gram	NH_3–N left	NO_3–N formed	Total N left	Total N loss	% Loss
1	10 0	0 315	0 24[illegible]	0 0[illegible]10	0 2738	0 0120	13 3
2	7 0	0 [illegible]211	0 1472	0 02[illegible]0	0 1692	0519	23 1
3	5 0	0 1[illegible]79	0 0888	0 0182	0 1070	0 0509	32 2
4	3 0	0 0[illegible]47	0 0272	0 0142	0 0414	0 0533	56 3
5	1 0	0 0316	Trace	0 0113	0 0113	0 020[illegible]	64 2

TABLE—III With ammonium phosphate

S N	Original Soln in c c	N content N gram	NH_3–N left	NO_3–N formed	Total N left	Total N loss	%Loss
1	7 0	0 1485	0 0714	0 0180	0 0894	0 0591	39 8
2	5 0	0 1061	0 0328	0 0072	0 0400	0 0661	62 3
3	2 0	0 0424	0 0069	0 0055	0 0124	0 0300	70 7

From the above results it can be easily seen that the original nitrogen taken and the nitrogen left after the experiments is not balanced but a considerable loss is recorded Hence Russell's statement is not confirmed and there is considerable loss of nitrogen in bacterial nitrification as in other natural conditions when nitrogenous manure is added to soil

Chemical Laboratories,
Allahabad University

References

1 Russell, E J Soil condition and plant growth 1932 Ed, pp 328
2 Dhar, Landon and Mukerji J Indian Chem Soc 1935, **XII**, 67
3 Dhar and Mukerji J Indian Chem Soc 1935, **XII** 756
4 Ditto J. Indian Chem Soc 1936, **XIII**, 555
5. Ditto J Indian. Chem Soc 1938 **XV**, 58
6 Ditto Nature, 1934, **134**, 572.
7 Russell E J 'Soil condition and plant growth. 1932 Ed., pp 361
8 Dhar Proc. K. Acad Nat. Amsterdam. **23** 308, 1920.

GROWTH OF YEAST IN VARIOUS ORGANIC AND INORGANIC FOOD MATERIALS

By

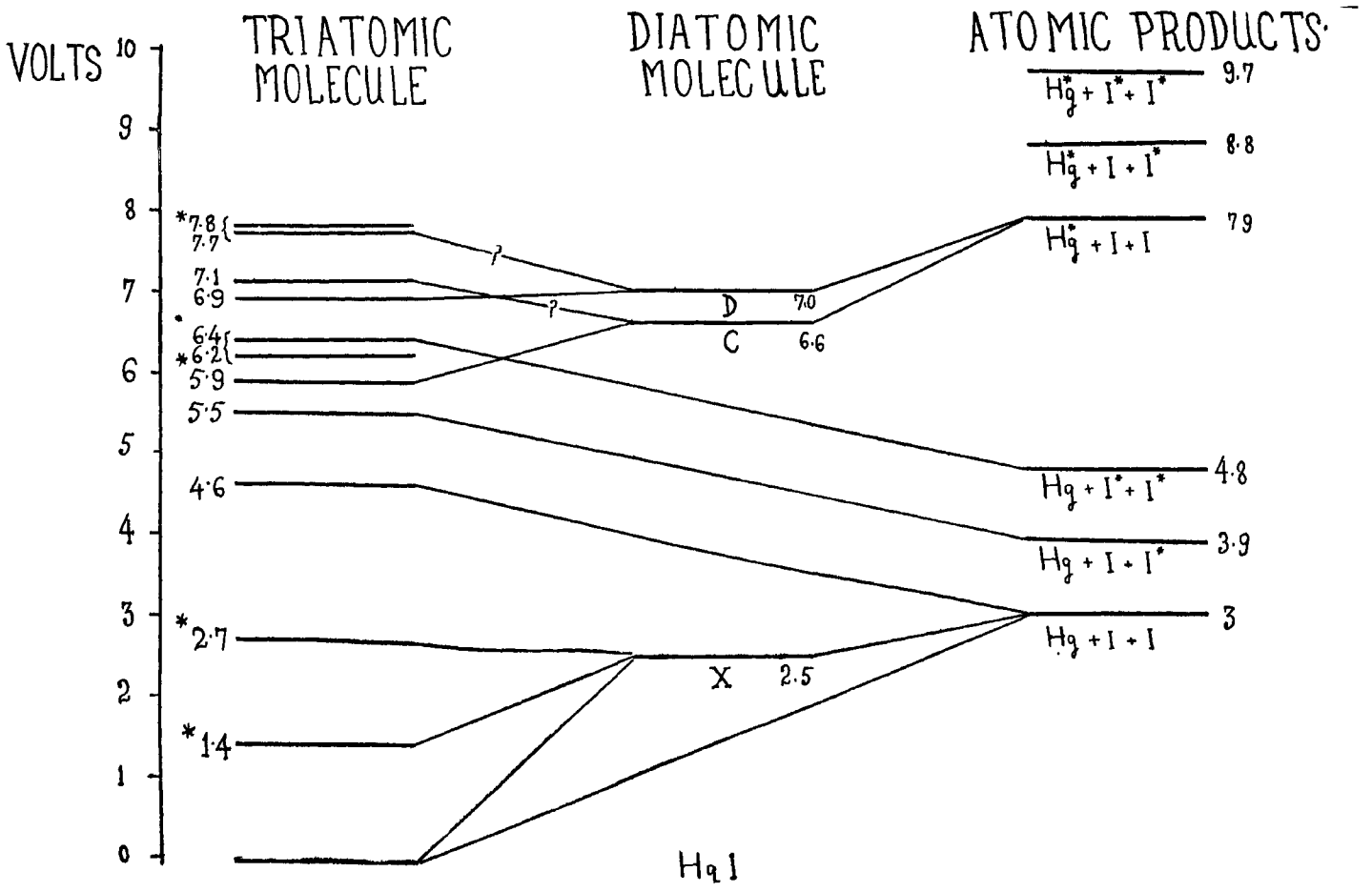
N. R. Dhar and Krishna Bahadur

Yeast is usually grown in sugars and malted barley. Recently we have developed a new technic by which yeast has been grown in solutions or suspensions of ethyl alcohol, starch, glycerol, oils gelatine, urea and even ammonium salts used as food materials. In this technic the yeast is grown in a suitable medium containing organic or inorganic food materials under sterile condition by passing a current of air which has been previously bubbled through strong sulphuric acid and distilled water.

It seems that in this process the starch or alcohol or glycerol or gelatine is partially oxidised to carbon dioxide and water and this energy of oxidation is utilised by the yeast for growth. A part of the organic compound is also utilised as food material for cell reproduction by the yeast.

With ammonium salts by passing air in presence of yeast the energy is obtained by the oxidation of the ammonium salts to nitrite and nitrates. In this case the carbon requirement for the growth of the yeast comes from carbon dioxide of the air or from the carbonate added to the yeast. In absence of oxygen or air growth of yeast in inorganic medium seems impossible. In case the alkalinity of the medium increases on passing air yeast can not multiply and even die.

The oxidations of sodium sulphite, sodium nitrite, sodium thiosulphate, powdered sulphur, sulphuretted hydrogen solution, are being tried for the growth of yeast in the inorganic medium. It seems that this technic may be useful to bacteriologists in growing microorganisms which develop with dicffiulty.


VOLTS
10
9
8
7
6
5
4
3
2
1
0
TRIATOMIC MOLECULE
DIATOMIC MOLECULE
ATOMIC PRODUCTS
*7·8
7·7
7·1
6·9
6·4
*6·2
5·9
5·5
4·6
*2·7
*1·4
?
?
D
7·0
C
6·6
X
2·5
Hg* + I* + I*
9·7
Hg* + I + I*
8·8
Hg* + I + I
7·9
Hg + I* + I*
4·8
Hg + I + I*
3·9
Hg + I + I
3
HgI

ENERGY LEVELS OF HgI AND, ITS PRODUCTS OF DISSOCIATION

By

Bishwanath Bhattacharya.

Department of Spectroscopy, Banares Hindu University

(Communicated by Prof. R. K. Asundi.)

Received on February 14, 1948.

Abstract

A review of the Spectroscopic work done so far in mercury iodide has been given and the energy levels of the molecules HgI_2, HgI and their atomic products of dissociation have been plotted with respect to the ground level of HgI_2 from the available thermochemical and spectroscopic data. A correlation of the levels of HgI_2 with the levels of the dissociation products has been suggested in the paper

Introduction

For a satisfactory explanation of the spectra of triatomic molecules it is obviously an advantage to possess as complete a knowledge of the spectra of their component diatomic molecules as possible. A definite correlation between the two spectra will then be possible thus leading to a better understanding of the structure of the di - and triatomic molecules which may be derived from the related products of dissociation. The importance of such information for the theories of valency is obvious In the case of multiatomic molecules such a procedure is much more difficult because the process of dissociation from multiatomic molecule to diatomic molecule will involve molecules of intermediate complexity about whose spectra very little is known with certainty at the present time Yet even here a large amount of experimental work mainly on the absorption spectra of multiatomic molecules in the vapour state has been utilized for such purposes of correlation A detailed account of such work is given in an article on "The Dissociation Spectra of Covalent Polyatomic molecules" by

*This is a revised form of a paper entitled "Energy levels of HgI_2 and its products of dissociation" read in the Joint Session of the Indian Academy of Sciences and National Academy of Sciences at Allahabad in December 1946.

Samuel (1943). From this point of view the mercuric iodide molecule HgI_2 suggests itself as a suitable molecule for investigation because both the absorption spectrum of HgI_2 and the emission spectrum of HgI have received considerable attention from workers.

It is known from Raman Effect and other data that the triatomic HgI_2 is linear in structure like CO_2 with a frequency of valence vibration of about 150 cm^{-1} **. The absorption spectrum of the vapour of this molecule gives rise to a large number of continuous bands The corresponding diatomic molecule HgI appears also to possess a large number of band systems which are observed only in emission and fluorescence but not in absorption.* Many of the emission bands are not yet systematised There is also no conclusive evidence to show whether the emitter of all these numerous emission bands is the diatomic HgI molecule or some of them are due to the triatomic HgI_2 molecule.

From experiments on electronic collision with mercuric iodide vapour Pavlov and Leipunsky (1926) found four critical potentials at 1 1 volts, 2 7 volts, 6.2 volts and 7 8 volts The first two critical potentials at 1 4 volts and 2 7 volts similar to the other two ought normally to exhibit themselves in the absorption spectrum of HgI_2 In other words the HgI_2 vapour should also show two absorption bands at wavelengths 8809A and 4568A corresponding to these two energy values No such absorption bands have been recorded so far

**Cf Kohlrausch: Der Smekal-Raman Effect, page 341 (1931 Edition)

*It is remarkable that none of the bands observed in emission or fluorescence with murcury iodide are observed in absorption. Similar situation is met with in mercury chloride. A suggestion to explain this is made by Wieland (1945). He has calculated the equilibrium constant K_p of the reactions $HgCl_2 = HgCl + \frac{1}{2}Cl_2$ $HgCl = Hg + \frac{1}{2}Cl_2$ and $HgCl_2 = Hg + Cl_2$ from the known free energy functions of Hg, Cl_2, HgCl and $HgCl_2$. The calculations go to show that even at very high temperatures the percentage of $HgCl_2$ molecules dissociating into HgCl and Cl is negligible and that most of HgCl molecules formed by such a dissociation are further dissociated into mercury and chlorine. It is also thought that similar results hold good for mercuric bromide and mercuric iodide.

in the absorption spectrum of murcury iodide It may be mentioned that Kondratjew (1930, 1931) has recorded a weak absorption band in the region 4800-3900A which on experimental grounds is, however, attributed by him to an ionic mercury iodide molecule Similarly Rao (1942) has given a very short notice of some discrete absorption bands in the region 4600-4100A which were recorded feebly in his experiments on the absorption of mercury iodide vapour and which according to him required further investigation

An attempt in the explanation of the absorption bands has been made by Butkow (1931) and Wieland (1932) already. Both of them attribute the absorption maxima to different processes of dissociation of HgI_2 into HgI and I. This is not very satisfactory. For example Wieland assumes four excited states of the HgI molecule within 4.5 e v. of the ground level whereas in reality only two are known for certain in this range.

In view of the above facts it was thought desirable to collect the known relevant data on the spectra of the two molecules with a view to their correlation. Experiments on the absorption spectrum of HgI_2 in the vapour and the solid states with a view to locate the expected band in the visible region which, however, have given a negative result are also briefly described.

A Survey of Previous Spectroscopic work on mercury iodide.

(A) Work in emission and fluorescence.

Peirce (1878) seems to have been the first person to undertake a spectroscopic study of mercuric iodide. He used Geissler discharge tubes containing the salt and on excitation found continuous bands in the region 4450 –4420 A in emission. Jones (1896, 1897) extended the observations in the ultraviolet. The latter observed diffuse bands from 4396 to 2538A. The intensity of the bands had a sharp maximum at 4441A and gradually diminished towards the violet. 143 band heads were grouped in three series. Strutt (1911) found that mercury lodide when excited by active nitrogen emitted violet light which consisted of bands. Strutt and Fowler (1912) closely investigated

this spectrum and observed a weak band at 3430A which is attributed to iodine, the atomic line 2536A of mercury and a band having a very great intensity in the range 1455 to 1390A and extending up to 3700A. Chapman (1914) introduced mercuric iodide into a discharge tube of the usual type fitted with aluminium electrodes, exhausted to about ·08 mm, sealed off and excited by the discharge from an induction coil. Without heating the tube the spectrum showed "the lines of mercury and iodine, besides those due to the residual air." After the tube was sufficiently heated to vaporize the mercuric iodide to a considerable extent, the character of the discharge radically changed, becoming an intense violet in colour. In addition to the lines of mercury and iodine there appeared "a brilliant band shading off towards both the red and the violet from about 4420A to 1450A."

Terenin (1926, 1927) observed a very bright visible fluorescence of mercuric iodide in the violet region when the vapour of the salt at low pressure was illuminated by a spark. The fluorescence bands had a rather sharp intensity maximum at about 1400A and a continuous falling off in intensity down to about 1000A. The lines which stimulated these bands were strictly confined to the region 2200 – 2100A. Primary dissociation of the triatomic molecule HgI_2 into an unexcited binary state HgI and an iodine atom which may or may not be excited was believed to take place in the course of the excitation of these fluorescence bands.

Wieland (1929) investigated the spectrum of mercury iodide activated in Geissler tubes in the range 7000A to 2300A. He divided the bands into three systems. The first type consists of 'band heads fitting a series formula of the Deslandres type but not satisfying Mulliken's isotope equation.' These bands were ascribed to the diatomic HgI molecule. The second type of bands have a triple structure and were originally ascribed to the triatomic molecule HgI_2. In the light of the later work of Wieland (1932) in fluorescence these bands were also ascribed to the diatomic molecule HgI. Band system of the third type consists partly of diffuse bands and partly of continuous spectra.

Wieland (1932) investigated the fluorescence bands stimulated by sparks from different metals and using suitable filters. The mechanism was associated with the following equations :-

$$HgI_2 + h\nu_a \rightarrow HgI^* + I$$

$$HgI^* \rightarrow HgI + h\nu_f$$

where $h(\nu_a - \nu_f) \geqslant$ the dissociation energy of $HgI_2 \rightarrow HgI + I$. Four band systems designated by B, C, D, E in the regions 4450-3500A, 3100-2800A, 2800-2650A and 2700-~2500A respectively were observed. The following approximate formulae were suggested for the fluorescence bands :

System C : $\nu = 32784 + (233{\cdot}3v' - 2{\cdot}25\, v'^2) - (124v'' - 10v''^2)$

System D : $\nu = 36130 + 175\, v' - 120\, v''$

For system B no analysis is given but the occurrence of the wave number intervals 120 cm^{-1} and 180 cm^{-1} is mentioned.

Prileshajewa (1932) observed two broad band systems in the regions 2114 to 2160A and 2168 to 2240A in an electrical excitation of mercury iodide and gave 125 cm^{-1} as the vibration frequency of HgI. Subbaraya, Rao and Rao (1937) measured the bands of system B in the first order of a 10 ft. concave grating on Rowland mounting. The spectrum was excited in emission in their experiments with a transformer discharge. The bands were found to be double-headed. The measurements of Subbaraya, Rao and Rao were found to be in close agreement with those of Terenin but were discordant with Wieland's values. The analysis of these bands as proposed by Subbaraya, Rao and Rao suggested the bands to arise due to an electronic transition between $a\,^2\pi$ and $a\,^2\Sigma$ state and showed that they have not got the same lower level as systems C and D. Sastry (1941, 1942) excited the mercury iodide bands in emission by both a transformer and an induction coil discharge and measured the bands of system E (in the region 2700- 2530) with a Hilger E_1 quartz littrow spectrograph He obtained in addition to the previously reported bands a new band system between 2530-2560A designated originally as system A and later by Rao, Sastry and Krishna murti (1945) as system F The system E was

found by Sastry (1942) to consist of two components and having a common final state and an electronic width of about 766 cm^{-1}, the band heads being given by the formulae.

$$\alpha_1 \text{ System: } \nu = 38786{\cdot}7 + \left[47{\cdot}7\,(v'+\tfrac{1}{2}) - 0{\cdot}8\,(v'+\tfrac{1}{2})^2\right] - \left[55{\cdot}2\,(v''+\tfrac{1}{2}) - 0{\cdot}8\,(v''+\tfrac{1}{2})^2\right]$$

$$\beta_1 \text{ System: } \nu = 38022{\cdot}1 - \left[44{\cdot}2\,(v'+\tfrac{1}{2}) - 0{\cdot}4\,(v'+\tfrac{1}{2})^2\right] - \left[55{\cdot}5\,(v''+\tfrac{1}{2}) - 0{\cdot}8\,(v''+\tfrac{1}{2})^2\right]$$

The vibrational frequencies involved in Sastry's α_1 and β_1 sub-systems in the band system E are of the right order of magnitude for the deformation frequency of the triatomic HgI_2 molecule. The deformation vibration of HgI_2 has, however, been found to possess a frequency of 33cm^{-1} (Sponer and Teller, 1941). It is therefore difficult to understand the above analysis of Sastry's bands.

The system F was attributed by Sastry to a transition $^2\Pi$ to $^2\Sigma$ showing four component heads and an electronic separation of 126 cm^{-1}. The analysis does not show any level in common with the other bands of HgI. For the Q_1 heads of system F the following vibrational formula has been given:

$$\nu = 39231{\cdot}1 + \left[98{\cdot}1\,(v'+\tfrac{1}{2}) - 2{\cdot}1\,(v'+\tfrac{1}{2})^2\right] - \left[92{\cdot}7\,(v''+\tfrac{1}{2}) - 2{\cdot}0\,(v''+\tfrac{1}{2})^2\right]$$

The systems C and D were reinvestigated by Rao, Sastry and Krishnamurti (1945) who have given the following vibration formulae:

System C:

$$\nu = 32730{\cdot}9 + \left[235{\cdot}6\,(v'+\tfrac{1}{2}) - 2{\cdot}16\,(v'+\tfrac{1}{2})^2\right] - \left[125{\cdot}9\,(v''+\tfrac{1}{2}) - 1{\cdot}07\,(v''+\tfrac{1}{2})^2\right]$$

System D:

$$\nu = 36269{\cdot}2 + \left[178{\cdot}0\ (v'+\tfrac{1}{2}) - 1{\cdot}14\ (v'+\tfrac{1}{2})^2\right] - \left[125{\cdot}70\ (v''+\tfrac{1}{2}) - 1{\cdot}10\ (v''+\tfrac{1}{2})^2\right]$$

The two systems are suggested to be the two components of a $^2\Pi$ to $^2\Sigma$ transition, the interval $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ being 3538 cm^{-1}. Rao and Rao (1946) have reported three band systems F_1, F_2, F_3 in the regions 2550-2500A, 2435-2385A and 2345-2300A respectively. F_1 comprises about 20 red degraded bands; F_2 consists of a succession of closely spaced bands degraded to the red and F_3 consists of about fifteen diffuse and mostly headless bands. According to them all the three systems have the same lower state, presumably $^2\Sigma$, as the systems C and D. They have also measured systems G and H (i.e. the systems originally obtained by Prileshajewa) under high dispersion and claim the existence of three distinct v'' progressions in G.

Bands of systems C and D have been unanimously ascribed by all the workers to the diatomic HgI molecule. Bands of system B are double headed with a doublet separation of the order of 60 cm^{-1} and having the vibration frequency of the emitter of the order of 270 cm^{-1} and 370 cm^{-1}. No electronic level common with systems C and D has been found for system B and there is no conclusive evidence to show whether the emitter of this band system is HgI_2 or HgI. Wieland interpreted these bands as having their final level the same as that of C and D systems. But Subbaraya, Rao and Rao do not agree with this view. Their data on the bands agree with those of Terenin but not with those of Wieland. The analysis of the new band systems F_1, F_2, F_3 recently proposed by Rao and Rao obtain the band origins by extrapolation since the (0, 0) bands according to these analysis are not observed. The electronic levels of the excited states of HgI obtained from these analyses have not been taken into account in this paper for the correlation of the energy states of HgI_2 and its dissociation products.

(B) Work in Absorption

Chapman (1914) photographed the absorption spectrum of a solution containing mercuric iodide, potassium iodide and water Potassium iodide was used to bring the mercuric iodide in solution A solution of potassium iodide in water gave no absorption Chapman claimed that there is a definite relationship between the emission and the absorption spectra, so that the vibrating system responsible for emision is responsible for absorption in solution also Mellor* states that Sheard and Morris (1916) found with mercuric iodide continuous regions or bands between 6072 and 5845 A, 5605 and 5535 A; 5195 and 5132A, 4828 and 4788A, 4506 and 4470A and 4450 and 4375A but it is not clear whether these bands were observed in emission or absorption Most probably these observations were made in the absorption spectrum of a solution of the compound Kondratjew (1930, 1931) observed a weak absorption in the vapour of mercuric iodide in the region 4800-3900A which increases in intensity with overheating of the vapour This absorption was attributed by him to an ionic mercuric iodide molecule The existence of this absorption is, however, doubtful as it has not been observed in any of the later investigations Butkow (1931) investigated the absorption spectrum of mercuric iodide both as a vapour and in solution in the range 7000A-1950A Three continuous absorption maxima at 2680A, 2240A and 2080A were observed The intense maximum at 2240A appeared at a pressure of ·015 mm and the maxima at 2080A and 2680A appeared successively as the pressure was increased Simultaneously with the appearance of the third maximum a continuous absorption with its limit at about 1950A appears On a further increase of pressure the limit of the last absorption shifted towards the longer wave-lengths and finally overlapped the absorption maximum at 2080A The limit of the maximum at 2680A was also found to shift to the longer wave-length side with increase of pressure and to reach 4400A at a pressure of 1—3 atmospheres The maxima were attributed by Butkow to dif-

* Cf Mellor A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol 4 (1923)

ferent states of dissociation of the molecule Thus the first and second maxima were attributed to dissociations with an unexcited HgI molecule as one product of dissociation in either case an unexcited iodine atom being the other product of dissociation The absorption spectra of the salt in solution clearly corresponded with that in the vapour state, the influence of the solvent being to diminish the number of maxima and to cause a slight shift of the position of the maxima Thus the solution of HgI in ethanol exhibited two absorption maxima at 2725A and 2175A, the first obviously corresponding to the maxima at 2680A and the second to the maxima at 2240A and 2080A in the vapour state Wieland (1932 extended the observations to the far ultraviolet region upto 1500A and found 7 to 8 absorption maxima Continuous absorptions with the intensity maxima at 2660A 2240A 1920A and 1720A and banded absorptions at 2080A and 1800A were observed The bands were seen to be specially sensitive to small pressure changes Thus the absorption band at 1920A appeared weakly at first at a pressure of 2 mms and with increasing pressure was found to gradually spread itself and overlap the bands at 1800A and 1720A The discontinuous structure of the bands at 2080A was found to develop between the pressures 2 4 mm From the short wavelength side commences a gradually broadening probably continuous region and above 1600A possibly a discontinuous region whose structure overlaps the many line spectrum of hydrogen arising out of the hydrogen tube used as a source of the continuous radiation Wehrli (1940) analysed the ultraviolet bands in the region 2066–2108A and obtained 156cm^{-1} and 33cm^{-1} as the frequencies of valence and deformation vibrations in the ground state of the molecule and 126 cm^{-1} and 30 cm^{-1} the corresponding values for the excited state

EXPERIMENTS ON THE ABSORPTION SPECTRUM OF HgI_2 IN THE VAPOUR AND THE SOLID STATES

The usual procedure of studying the absorption spectrum was adopted in the present experiments A sealed glass tube 9 3 cms long containing mercuric iodide in the presence of air was used for

absorption. An electric bulb or the positive crater of a carbon arc was used as the source of continuous radiations. The absorption cell could be heated to different temperatures by enclosing it in an electric furnace in the course of the experiments. The furnace was calibrated for different current strengths and the temperature of absorption cell estimated from a knowledge of the adjusted current strength and the calibration curve. Several spectrograms taken with a Hilger's Constant Deviation Glass Spectrograph failed to register any characteristic absorption by the mercuric iodide vapour. Experiments were then repeated by replacing the glass absorption cell by a quartz cell 10 cms long. The latter had a side tube which was plugged with glass wool after being filled with mercuric iodide. No characteristic absorption of the mercuric iodide vapour in the visible region was obtained. The well known iodine absorption bands were observed to appear at about 300°C and to become more and more prominent at higher temperatures. These bands do not overlap the region of the expected band (4568A) in the visible region. The absorption bands in the near ultraviolet region, however, easily obtained on a E_1 Hilger's Quartz Spectrograph when the quartz cell was used, the source of continuous radiations in this case being a locally prepared Hydrogen discharge tube with a quartz window. It has been observed that the absorption bands are practically absent if the higher temperatures are attained from room temperatures. They appear very clearly for the range of temperature 270-300°C only if the cell is first of all heated to a temperature higher than 400°C and then cooled to the required lower temperature in the range 270 – 300°C. No new band was observed in the quartz ultraviolet region but the plates were utilised to measure the total width of the absorption bands along with their maxima. These data are given in the following table which also records the data obtained by Wieland.

Table I

Absorption Region		Absorption Maxima	
Wavelength	c. v.	Wavelength	c. v.
2600 – 2950A	4·74 – 4·18	2700A	4·6
2330 – 2170A	5·29 – 5·68	2250A	5·5
2075 – 2090A	5·94 – 5·90	2080A	5·9
		* 1920A	6·4
		1800A	6·9
		1720A	7·1
		1600A	7·7

A further attempt to locate the expected absorption band in the visible region was made by using glass and quartz plates lightly dusted with mercuric iodide and an electric bulb or the hydrogen discharge tube as the source of continuous radiations. These experiments also yielded negative results. The near infrared region where an absorption band at 8809A is expected to lie could not be photographed as suitable plates were not available.

Discussion

Assuming that all the observed absorption maxima belong to HgI_2 and represent transitions from its ground state to various excited electronic levels, the positions of these levels are located by the energy values tabulated in column 4 of Table I. HgI_2 possesses two more levels indicated by collision experiments. In the diatomic

* Outside the range of the present experiments.

molecule HgI, so far two electronic levels in addition to the ground state are known these being at 1.1 and 4.5 e.v. relatively to the ground level. There do not appear to be any energy level lower than 4.1 e.v., the reported new bands involving levels higher than 4.5 e.v. The positions of the energy levels of HgI and of the atomic dissociation products relative to the ground level of HgI_2 may be obtained if the heat of formation (or dissociation) of the two molecules in their normal states are known.

Now various methods are available to estimate the heat of formation (or dissociation) of a molecule. Thus the heat of formation of HgI molecule from its constituent atoms may be estimated from the thermochemical value of the heat of formation as is obtained from various reactions and other available data making use of the Born Cycle. It can also be obtained both in its normal and excited states making use of the analysis of the emission bands ascribed to the molecule. Here again several methods of extrapolation are available. The values obtained by all these methods for HgI in its normal and excited states are shown in Table II.

*Table II**

Level	Thermo-chemical	Linear Extra-polation	Graphical Extrapolation	Mean
X (Ground)	·58	·16	·52	·5
		·44	·51	
C (Excited)	...	·8	·85	·83
D Do	...	·86	93	·9

*All required thermochemical data in the present calculations are taken from Landolt-Börnstein· Physikalisch Chemische Tabellen (1935 and earlier editions) except the heat of sublimation of HgI which is taken from Sponer. Molekulspektren und ihre Anwendung Auf Chemische Probleme. The spectroscopic data are taken from Rao, Sastry and Krishnamurti. In calculating the heat of formation of HgI_2, data concerning both varieties red and yellow of HgI_2 are used. The energy difference between the two varieties is about 3 KCal/Mol (=0·13 e.v.) and is ignored.

Only thermo-chemical methods are available to estimate the heat of formation of HgI_2 from its constituent atoms and the mean value calculated from observations of different observers taken from literature is 3·0 volts.

Making use of the absorption, collision and emission data so far known as detailed above and the calculated energies of dissociation we shall arrive at the energy level diagram shown in Fig I for the HgI molecule and its dissociation products. The heat of formation of HgI_2 from the constituent atoms in their normal states being 3 e.v. the level of the dissociated atoms Hg (^1S) and 2I ($^2P_{3/2}$) is plotted 3 volts above the ground level of HgI_2. The next plausible excited states of the dissociated atoms obviously correspond to one and two excited states of the iodine atom and are plotted assuming the first excitation potential of the iodine atom to be 9 volt** Still higher excited states of the dissociated atoms correspond to $Hg^*(^3P_1)+I+I$, $Hg^*(^3P_1)+I^*(^2P_{1/2})+I$ and $Hg^*(^3P_1)+I^*(^2P_{1/2})+I^*(^2P_{1/2})$ where Hg* and I* represent the excited states of Hg and I respectively. They are plotted assuming the first excitation potential of Hg to be 4·9 e.v.**. The dissociation energy of HgI in its normal state being 5 e.v. the ground level of HgI is plotted with respect to the ground level of HgI_2 by putting it ·5 volt below the level of Hg+I+I. The two excited states of HgI are obtained from a knowledge of the (0, 0) bands in systems C and D viz., 32785 cm^{-1} (= 4·05 e.v.) and 36295 cm^{-1} (= 4·48 e.v.).

All the three levels X, C and D of the diatomic molecule correspond to the attractive states of the molecule possessing potential energy curves with a minimum. Each of them may also represent a repulsive state for the triatomic molecule HgI_2. This seems to be much more probable for the level X which belongs to the ground state of the diatomic molecule than to the levels C and D which belong to its excited states. Among the levels of the atomic products the first one at 3 e.v. no doubt belongs to the ground states of

**Cf. Bacher and Goudsmit : Atomic Energy States.

both the diatomic and the triatomic molecules and hence definitely possesses a state of the attractive type Similarly the one at 7 9 e v can be correlated within the limits of experimental and extrapolational error with the two excited states C and D of HgI Extrapolation of C gives for the energy of dissociation 8 3 e v while that for D gives 9 e v (vide Table II) These give respectively 7 43 and 7 9 for the position of the level of the atomic products which are in fair agreement with the calculated value 7 9 It is, therefore, certain that the level at 7 9 e v, also possess s a state of the attractive type For none of the other four levels of the atomic products can this be said with certainty at the present state of our knowledge In contradistinction to this, however, every one of these six levels will be possessing one or more states of the repulsive type It is these repulsive states and the three states of the diatomic molecule which correlate with electronic energy states of the triatomic molecule in some way which is to be determined To do so we come to that part of the energy diagram which belongs to the excited states of the triatomic HgI_2 We have here to bear in mind the following The determination of the position of the excited energy levels of multiatomic molecules probably because they possess very few stable excited states—is often not possible In the first place most of the absorption bands are continuous This means that the maxima represent positions on the repulsive curves belonging to the excited molecule, which are directly above equilibrium position of the normal molecule If the repulsive curves are almost flat then the maxima would represent the positions of the levels of the dissociation products of the excited molecule, otherwise they include also an additional amount of kinetic energy, which depends on the steepness of the curves In the few cases where band absorption is observed unless the origin of the band can be located it is not possible again to determine the position of the energy level In this case, however, the particular potential energy curve for the molecule is an attractive one exhibiting pronounced minimum which can be located if the bands are analysed Thus whereas band absorption has the

possibility of yielding the information about the energy levels continuous absorption gives the possibility of determining the energy of the dissociation products of the excited states Collision data also represent a mixture of both types of excited states, repulsive as well as attractive, of the molecules This is true as much for diatomic molecules as for multiatomic ones Only in the case of atoms, do the collisions and absorption data give just the energy levels of the excited atoms

Among the energy values of the triatomic molecule determined by critical potentials and absorption maxima those of 6 2 (coll and 6 4 (abs) seem to be identical as also those of 7 8 coll) and 7 7 (abs) These are therefore, bracketed in the figure We thus have nine energy values of the excited HgI_2 molecule Wieland has observed structure in the absorption maxima at 5 9 and 6 9 e v Under the dispersion used in our experiments we could not detect any structure in the band at 5 9 e v but it is particularly a very sharp and narrow band Wehili (1940) has analysed this band system and obtained the vibration frequencies of the triatomic molecule both in the ground state and excited state corresponding to this absorption The region of absorption observed by him is wider than that observed in the present experiments The conditions of his experiments could not be ascertained as his paper was not available These two values therefore very probably represent stable excited energy states of the triatomic molecule having attractive potential curves whose dissociation limits lead to C and D respectively of the diatomic molecule HgI or to the level at 7 9 of the separated atoms Similarly the value of 1 4 probably represents an excited energy state of the molecule because there is no energy level to which it can be correlated either in the diatomic molecule or in the separated atoms with a value less than 1 4 e v If the collision data are correct in establishing this level, it can be predicted with considerable confidence that there will be a b nded absorption for HgI_2 in the near infra-red region†

† However dissociation of the HgI_2 into I_2 and Hg may also be the process brought about by collision This process requires just 1 42 e v

The remaining six values almost certainly represent only positions directly above the equilibrium position in the ground state on the repulsive potential curves belonging to excited HgI Of these the one at 2 7 e v can go over only to the level X of the diatomic molecule at 2 5 e v

Among the remaining five levels the three levels at 4 6, 5 5 and 6 4 e v are separated by the doublet separation of the Iodine atom viz 0 9 e v and hence can be correlated to the levels at 3, 3 9 and 4 8 e v of the atomic products with considerable confidence From a glance at the energy level diagram it can be seen that such a correlation suggests the absorption bands corresponding to these energy levels to have widths of roughly the same order The widths of the bands at 4 6 and 5 5 e v have been found to be 56 and 39 e v respectively in the present experiments whereas the width of the band at 6 4 e v (which is outside the range of the present experiments) is not recorded

Wieland observed some structure in the absorption band at 7 e v but this has not been definitely established due to the overlapping of the many line spectrum of hydrogen with this absorption region If the observation is correct there should be a stable level of the triatomic molecule at 7 8 e v going over to some higher state of the dissociation products The latter state may be any one of the states 8 8 and 9 7 e v of the atomic products, correlation with 7 9 e v being not very probable due to its small difference in energy with the triatomic level considered No definite correlation for this stable state – if it exists at all – can be given without further work on the corresponding absorption band The explanation of the excitation of the fluorescence bands of system D would necessitate the existence of a repulsive state of the triatomic molecule at 7 7 e v going over to the state D of the diatomic molecule This correlation should however be considered as tentative the level D of the diatomic molecule being an excited state

Now the level at 7 1 e v remains to be explained The possibility of an intermediate level between X and C in the diatomic molecule is not very sure The analysis of the bands of system B by various workers locate one or more levels between X and C Different workers do not agree with one another in their analysis and measurements of this band system Moreover there is no conclusive evidence for the identification of the emitter of this band system with the diatomic HgI molecule Further experimental work is needed to unequivocally decide about this point The absorption band at 7 1 e v being a continuous one there is a repulsive state associated with it The only known level to which it can go is the level C of the diatomic molecule This correlation should also be regarded as tentative The discrepancy in the minimum values for the frequencies of the radiations exciting the fluorescence bands of systems C and D as found from this correlation with those experimentally observed by Wieland may be ascribed to the fact that the accuracy of the observations is not great, the wavelengths of the exciting radiations having been separated out with the help of suitable filters

ACKNOWLEDGMENT

I take this opportunity of expressing my gratefulness to Dr R K Asundi for his guidance, help and encouragement throughout the course of the work Thanks are due to the authorities of the Benares Hindu University for the award of J K Research Fellowship, Watumull Foundation for a Fellowship and the Akhil Bharatiya Arya (Hindu Dharma Seva Sangha, Delhi for one of the Lala Kamlapat Singhania Scholarships for varying periods while the work was in progress

References

Butkow K (1931) Zeit f Phys 71 678

Chapman A K (1914) Phys Rev (2) 4 28

Jones A C (1896), Dissert Erlangen

Jones, A C (1897) Wiedem Ann 62 30
Kondratjew V (1930) J Phys Chem Moskau 1, 34
Kondratjew, V (1931), Zeit f Phys Chem B, 11, 470
Pavlov, V I. and Terpunsky A I (1926) Nature, 118, 843
Peirce, B O (1878) Wiedem Ann 6, 597
Prileshajewa N (1932), Phys Zeit d Sowjet Union, 1, 189
Rao, A L S (1942) Ind J Phys 16 393
Rao, K R, Sastry M G and Krishnamurti V G (1945), Ind J Phys 18, 323
Rao V R and Rao, K R (1946 Ind J Phys 29, 148
Samuel, R (1946), Rev Mod Phys 18 103
Sastry, M G (1941), Curr Sc 10, 521
Sastry, M G (1942), Proc Nat Inst Sc Ind, 8 289
Sheard, C and Morris, C S (1916), Ohio J Sc 16 113
Sponer H and Teller, E (1941) Rev Mod Phys, 13, 108
Strutt R J (1911), Pro Roy Soc A, 85 219
Strutt R J and Fowler A (1912) Pro Roy Soc A 86, 105
Subbaraya, K S Rao, B N and Rao, N A N (1937), Proc Ind Acad Sc A 5 365
Terenin, A (1926) Nature 118 843
Terenin, A (1927), Zeit f Phys 44, 713
Wehrli, M (1940), Helv Phys Acta 13, 153
Wieland, K (1932), Zeit f Phys, 76, 801
Wieland K (1945), Nature, 156, 504

INFLUENCE OF TEMPERATURE ON NITROGEN FIXATION IN STERILE AND UNSTERILE CONDITIONS

PART I

By

N R Dhar and R C Kapoor

While it has long been believed that in the protein bodies of certain organisms existing in the soil, nitrogen of the air becomes incorporated leading to enrichment of soil nitrogen[1], Dhar and co-workers have produced strong evidence in favour of a purely physico chemical view of nitrogen fixation in soil

Not much work have been done regarding the influence of temperature on nitrogen fixation We have under taken a systematic investigation on nitrogen fixation at different temperatures on the addition of energy materials under sterile and unsterile conditions

Experimental details The soil or purified aluminium oxide or zinc oxide mixed with the energy rich substance was kept in 600 cc pyrex flasks, plugged with absorbent cotton wool and kept under 16 lbs pressure for one hour for sterilization After every month the flasks were opened, moisture contents made up to 10% and resterilised In each case the soil was tested for Azotobacter by the plate method and no colony growth was observed even after seven days incubation at 35°

In these experiments 100 gms of well seaved soil was taken in each case and 2 gms of cane sugar was mixed with it as the energy material Moisture content was made to 10% in every case These sterilized flasks were incubated at different temperatures in the dark One such flask was exposed to daylight for seven hours daily for comparison The temperature of the incubated flasks varied from 7° to 60° Some experiments for comparison were also carried out in unsterile condition

The carbon and nitrogen estimations were done by the method of Robinson, McLean and Williams[1] by heating 5 gms. of well dried and powdered soil with 30 ccs. of pure concentrated Sulphuric acid, 5 gms. of fused potassium sulphate and a few crystals of pure copper sulphate for four hours. The ammonium sulphate thus formed was estimated by treating an adequate part of it with magnesium oxide and 100 ccs water and distilled for six hours in a water bath. At the same time a current of air purified by passing through a solution of ferrous sulphate and sulphuric acid was aspirated. The ammonia was absorbed in two conical flasks containing pure dilute sulphuric acid. The ammonia obtained was estimated colorimetrically by nesslerization in a Duboscq colorimeter.

The total carbon was determined simultaneously by absorbing the sulpur dioxide produced at the time of charring by a standard iodine solution, the excess of which was titrated against a standard thio-sulphate solution.

The results with cane sugar are as follows:

I—100 gms soil + 2 gms cane sugar (Sterile)
Carbon introduced—0 8 % approximately
Time of exposure—342 days (5-3-47 to 10-2-48)

Method of Exposure	5-3-47		22-5-47		8-11-47		10-2-48		Carbon oxidised %	Nitrogen fixed per gm. of carbon oxidised (mgm,)
	Total C %	Total N %	Total C %	Total N %	Total C %	Total N %	Total C %	Total N %		
Exposed to Light ..	1·220	0·0385	0·938	0 0429	0 658	0·0468	0·594	0·0476	0·626	14·5
7° (Dark) ..	1·220	0·0385	1·086	0·0386	0·860	0·0385	0·788	0 0385	0·432	Nil
30 (Dark) .	1·220	0·0385	1·012	0·0404	0·728	0·0421	0·668	0·0424	0·552	7·0
35° (Dark) .	1 220	0 0385	1·007	0·0404	0·709	0·0426	0·646	0·0430	0·574	8·6
40° (Dark) ...	1 220	0·0385	1 035	0·0393	0·792	0·0402	.	...	...	3·9
45° (Dark) ...	1 220	0·0385	1·080	0·0388	0·813	0 0393	0·754	0·0394	0·466	1·9
60° (Dark) .	1·220	0 0385	1·095	0 0384	0 838	0 0384	0·779	0·0384	0 441	Nil

Exactly similar experiments were carried out with cowdung as energy material. However, one set in unsterile condition was also kept and the results are as follows :

II—100 gms. Soil + 10 gms. Cowdung (Unsterile)
Carbon introduce = ·8% Approximately
Time of Exposure 24-12-'46 to 19-1-'48

Method of Exposure	24-12-46		5-4-47		26-8-47		19-1-48		Nitrogen fixed per gm. of carbon oxidised
	Total C %	Total N %	Total C %	Total N %	Total C %	Total N %	Total C %	Total N %	
Exposed to light ...	1·165	0·0742	0·876	0·0808	**0·816**	**0·0810**	0·780	0·0792	19 5 mg.
7° (Dark)	1·158	0 0740	1 060	0·0740	1·024	0 0740	0 968	0·0742	nil
25° (Dark)	1·162	0·0742	0·923	0 0764	0 835	0 0770	0·804	0 0772	8·4 mg.
35° (Dark)	1·160	0·0742	0·898	0 0772	0·822	0 0779	0 781	0·0780	10 0 mg.
40° (Dark)	1·162	0 0740	0·928	0 0752	0 857	0·0754	.	...	4·0 mg.
60° (Dark)	1·161	0·0741	1·116	0 0740	1·084	0·0740	0·988	0·0740	nil

Discussion —From the foregoing results it is clear that the optimum temperature for carbon oxidation and nitrogen fixation is 35° in dark The fall in carbon oxidation and nitrogen fixation after 35° is more marked than before 35 There seems to be no nitrogen fixation at 7° and 60° though carbon oxidation takes place to some extent It is interesting to note that similar observations of carbon oxidation in solutions have been obtained by Dhar[4] while studying 'The influence of temperature on the slow and induced oxidation of glucose in the dark' It is clear from the observations tabled there that "the velocity of the oxidation of glucose goes on increasing upto a certain optimum temperature, which lies between 30° and 40°

The conclusions formulated above are made clear by the following table

I Soil + Cane sugar
Carbon introduced = 0 8 % approximately
Time of exposure = 312 days

Temp		Carbon oxidised		Efficiency of nitrogen fixation	
(i) Light	→	0 626%	→	14 [illegible]	m gms
(ii) 7 dark	→	0 43[illegible]%	→	nil	,,
(iii) 30° ,,	→	0 552%	→	7 0	,,
(iv) 35° ,,	→	0 574%	→	8 6	,,
(v) 45° ,,	→	0 466%	→	1 9	,,
(vi) 60° ,,	→	0 441%	→	nil	,,

II Soil + Cowdung (Sterile)
Carbon introduced = 8% approx
Time of exposure = 245 days

(i) Light	→	251%	→	17 5	m/gms
(ii) 7° Dark	→	130%	→	nil	,,
(iii) 25° ,,	→	186%	→	9 1	,,
(iv) 35° ,,	→	221%	→	9 9	,,
(v) 40° ,,	→	164%	→	5 3	,,
(vi) 60° ,,	→	073%	→	nil	,,

III Soil + Cowdung (Unsterile)
Carbon introduced = 8% approx
Time of exposure = 245 days

(i) Light	→	349%	→	19 5 m gms		
(ii) 7° Dark	→	134%	→	nil	,,	
(iii) 25° ,,	→	327%	→	8 6	,,	
(iv) 35 ,,	→	338%	→	10 9	,,	
(v) 10° ,,	—→	305%	→	4 6	,,	
(vii) 60° ,,	—→	077%	→	nil	,,	

Dhar and Seshacharyulu also carried on some experiments on nitrogen fixation at different temperatures in unsterile condition In their experiments glucose was used as the energy material The results of carbon oxidation and the efficiency of nitrogen fixation in equal time at different temperatures are given below

Temperature	Time of exposure 27-2-37 to 13-5 37 Carbon oxidised	Efficiency of Nitrogen fix
(i) Light	670 %	13 1 m gms
(ii) 10°-12°	369%	nil ,,
(iii) 25°	385%	5 4 ,,
(iv) 30°	488%	6 7 ,,
(v) 35°	555%	8 1 ,,
(vi) 40°	374%	4 8 ,,
(vii) 45°	327%	4 2 ,,
(viii) 50°	254%	1 9 ,,
(ix) 60°	237%	nil ,,

It is significant to note that the results obtained by using glucose in unsterile conditions are similar to those obtained by us in sterile conditions by using different energy materials Here also the carbon oxidation and the efficiency of nitrogen fixation is greater in light than

at any temperature in dark which goes to prove that it is light and not the higher temperature, that increases the fixation in exposed soil sets.

There was no fixation at 7° even in the unsterile sets though some Azotobactor growth was there which shows that the activity of Azotobacter ceases at that temperature which is in accordance with previous experiments.

In our experiments it is noted that the velocity of carbon oxidation and the efficiency of nitrogen fixation falls with time. Though the velocity of carbon oxidation varies with the nature of energy material, the amount of nitrogen fixed per gram of carbon oxidised remains nearly the same for all the energy materials at a constant temperature. This goes to prove that the energy required for nitrogen fixation comes from the energy liberated by the oxidation of carbon.

These results are best explained in the light of adsorption of gases on Solid Surfaces. The normal adsorption due to vander Waal's forces decreases with rise of temperature while the activated adsorption, since it is chemical in nature, increases with temperature just like the velocity coefficient of ordinary chemical reactions requiring a high activation energy. This explains as to why we do not get any appreciable fixation at 7°. As the temperature is increased a condition is obtained in which the rate of the activated process becomes appreciable and so the resulant total adsorption begins to increase with rise of temperature as takes place below 35. This increase continues over a range of temperature, until the normal effect of temperature on the amount adsorbed, apart from its rate, brings about a decrease, as takes place above 35°.

In our experiments the actual temperature when the rate of activated adsorption becomes appreciable lies somewhere between 7° and 25°. The activated process reaction stops at a temperature little above 45°. Further experiments on efficiency determination at the in between temperatures are in progress.

The energy of activation of the reaction

free nitrogen $\longrightarrow$ fixed nitrogen

has been calculated as follows

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2}$$

Integrating at two different temperatures

$$\log_e \frac{k_2}{k_1} = \frac{E}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

where k_1 and k_2 are the elocity constant of the reaction at temperature T_1 and T_2 respectively

$$\text{Hence } E = \frac{2{\cdot}303 \log_{10} \frac{k_2}{k_1} \times R \times T_1 \times T_2}{T_2 - T_1}$$

As the velocity constants are proportional to the products formed, so here taking the cane of cane sugar at 30° and 35°

$$E = \frac{2{\cdot}303 \log_{10} \frac{45}{39} \times 1{\cdot}99 \times 308 \times 303}{308 - 303}$$

Since 45 and 39 are the amounts of nitrogen fixed at 35° and 30° respectively.

$$E = 5300 \text{ calories}$$

References

I Waksman "Soil Microbiology.

II Dhar "Nature" 151 (1943), 590.

III Journal Agric. Sci **19**, 315, 1929.

IV Dhar "The influence of temperature on the slow and induced oxidation of glucose in the dark".

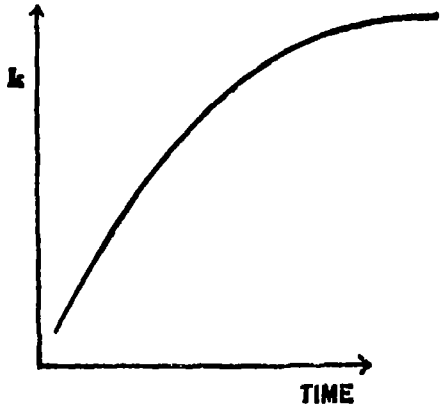
(Journ Indian Chem. Society, Vol. **19**, No. 7, 1942).

Calculation of Velocity Constant in Presence of Heterogeneous Auto-catalyst.

By

BAL KRISHNA AND S GHOSH

In two previous communications (2, 3) the present authors have studied the kinetics of reduction of silver acetate and silver tartrate by resorcin wherein it has been shown that the value of the velocity constant increase with time reach a maximum and then begin to decrease This can be well represented by the following curve



The ascending portion of the curve points to the autocatalytic nature of the reaction the fine particles of silver produced acting as heterogeneous catalyst The descending portion of the curve points to the decrease in catalytic activity due to decrease of catalytic surface caused by gradual coagulation of fine particles of silver It requires a high mathematical ingenuity to devise a formula which shall give constant values for the velocity constant since the catalysis depends upon total surface which is a complicated function of the number and size of the particles of silver both of which are in a state of constant flux We have failed to devise any such formula but have worked out an equation which gives constant values of the velocity constant for the ascending portion of the curve in the following reaction

$$Fe + Ag \rightarrow Fe + Ag$$

This reaction had been previously studied by Robert and Soper (4) and Dhar (1) but the order of the reaction has not been determined. Indeed Robert and Soper have pointed out that the reaction is instantaneous as in mostionic reactions and not amenable to kinetical treatment. We find however, that it proceeds regularly if we take into consideration the catalytic activity of colloidal silver (details to be published later).

Now it was Ostwald (see A Text Book of Physical Chemistry by Glasstone) who for the first time studied autocatalysis on a kinetical basis. In the hydrolysis of an ester eg. methyl acetate, the acetic acid produced works as a catalyst. Let a be the concentration of the ester and b of the acetic acid present initially and let x be the amount of ester hydrolysed after time t, then the rate of hydrolysis at any time is given by

$$\frac{dx}{dt} = k\,(a-x)\,(b+x). \qquad \ldots \quad (1)$$

On integrating in the usual way this gives

$$K = \frac{1}{t\,(a+b)}\, l\,n\, \frac{a(b+x)}{b(a-x)} \qquad \ldots \quad (2)$$

which has been confirmed by Ostwald.

This (2) equation can not be applicable in our case since our reaction is bi-molecular one. We have started with the assumption that for the ascending portion of the curve the colloidal silver produced works as a homogeneous catalyst and is proportional to x, which is the amount of silver formed. Then

$$\frac{dx}{dt} = k_1\,(a-x)^2 + k_2\,(a-x)^2 x \qquad \ldots \quad (3)$$

But since the term $k_1\,(a-x)^2$ is negligible as the uncatalysed reaction is very slow we can write

$$\frac{dx}{dt} = k\,(a-x)^2 x \qquad \ldots \quad (4)$$

Integrating this we get

$$kt = \frac{1}{a^2}\, l\,n\, \frac{x}{a-x} + \frac{1}{a(a-x)} + c, \qquad \ldots \quad (5)$$

where C is the integration constant. It is not possible to find out the value of C. When we put $X=0$ when $t=0$, we find that the term $\frac{x}{a-x}$ becomes 0.

The same flaw is observable in Ostwald's equation (2) When b is zero i.e., when acetic acid present initially is zero then the term $\frac{a(b+x)}{b(a-x)}$ becomes infinity, and the whole equation becomes meaning less. This can be avoided if we integrate between two time limits when the integration constant disappears. Now

$$\frac{dx}{at} = k\,(a-x)^2 x$$

and integrating between t_2 and t_1 we get

$$\int_{x_1}^{x_2} \frac{dx}{(a-x)^2 x} = k \int_{t_1}^{t_2} dt$$

$$\text{or } \frac{1}{a_2}\int_{x_1}^{x_2} \frac{dx}{x} + \frac{1}{a_2}\int_{x_1}^{x_2} \frac{dx}{(a-x)} + \frac{1}{a}\int_{x_1}^{x_2} \frac{dx}{(a-x)^2} = k\int_{t_1}^{t_2} dt$$

$$\text{or } k\,(t_2-t_1) = \frac{1}{a_2}\left\{ ln\,\frac{x_2(a-x_1)}{x_1(a-x_2)} \right\} + \frac{1}{a}\left\{ \frac{1}{a-x_2} - \frac{1}{a-x} \right\} \qquad \ldots (6)$$

We find that the equation (6) works well in our case as the following table will show.

t_2	t_1	k
130	50	0·01738
80	30	0·01741
50	30	0·01818
120	80	0·01964
80	50	0·01905

These values are a great improvement over the following values of the constant which have been worked out with usual bimolecular formula viz.,

$$K - \frac{1}{t} \frac{x}{a(a-x)}$$

t	k
30	0·001526
50	0·002350
80	0·003287
120	0·008268
180	0·011310

The equation (6) represents a third order reaction although a new type of third order reaction.

Physical Chemistry Laboratory
Allahabad University (India)

References

1. Dhar, *Proc. K Akad Wetensch.* (Amsterdem, 299, **23** 1920).
2. Krishna and Ghosh, (*J. Physi. Chem* **51**, 1130, 1947).
8. Krishna and Ghosh, paper read at the joint session of Indian and National Academy of Science, India, Dec. 1946.
4. Robert and Soper, (*J. Chem. Soc.* 2004, 1932).

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1948

PART III] SECTION A [VOL. 17

A NOTE ON HIGH FREQUENCY CURRENT DENSITY IN A HOLLOW CYLINDRICAL CONDUCTOR.

BY

SANTI RAM MUKHERJEE

ENGINEERING COLLEGE, BANARAS HINDU UNIVERSITY.

Received on April 2, 1948.

Hollow cylindrical conductors have lately gained very wide application in Radio Engineering. Due to their non-radiating properties, they are conveniently used in connection with ultra-short and micro-wave transmission lines, wave-guides, etc., particularly for radar and television purposes. It is often found necessary to know the current density along the radius of such a conductor, specially to detect the formation of stationary waves along the cross-section of the tube. The current-density for steady sinusoidal current (1) can be calculated by Bessel functions, and in the present communication, the solution has been obtained for varying high frequency current following through the conductor For the purpose of relaxed oscillations, a solution has also been obtained for linear variation of current with time

If μ be the permeability, ρ the resistivity of the material of the cylindrical conductor, the value of current density g at any radius r can be obtained from the differential equation,

$$\frac{\partial^2 g}{\partial r^2}+\frac{1}{r}\frac{\partial g}{\partial r}-\frac{4\pi\mu}{\rho}\frac{\partial g}{\partial t}=0 \qquad . \quad . \quad . \quad (1)$$

For steady sinuisoidal high frequency current, it may be assumed that $\frac{\partial g}{\partial t}$ $j\omega g$, where ω is the pulsatance of the current. Then the solution of (1) is given by

$$g = \{A\, I_0\, (kr\sqrt{j}) + BK_0\, (kr\sqrt{i})\}\, (\cos \omega t \times j \sin \omega t) \quad . \quad . \quad (2)$$

Where I_0 and K_0 represent ber-bei anc ker-kei functions respectively.

In case the high frequency current is varying, the solution of equation (1) may be obtained as shown below.

Let $g = g_1\, g_2$ where $g_1 = f_1\,(r)$ and $g_2 = f_2\,(t)$.

Then from (1), $g_2 \left(\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg_1}{dr}\right) - A_1\, g_1 \frac{dg_2}{dt} = 0$, where $A_1 = \frac{4\pi\mu}{\rho}$

$$\text{or } \frac{1}{g_1}\left(\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg_1}{dr}\right) - \frac{A_1 dg_2}{g_2\, dt} = 0$$

This is satisfied if we write

$\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg_1}{dr^2} - kg_1 = 0$ and $\frac{dg_2}{dt} = \frac{k}{A_1}\, g_2$, k being an arbitrary constant.

Now $$\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg_1}{dr} \quad kg_1 = 0. \quad . \quad . \quad . \quad (3)$$

Will give rise to I_0 and K_0 functions

From $\frac{dg_2}{dt} = \frac{k}{A_1}\, g_2 = (-\alpha + j\omega) g_2$ where $\frac{k}{A_1} = -\alpha + j\omega \quad . \quad . \quad . \quad (4)$

We get $g_2 = c_1\, e^{-\alpha t}\, (\cos \omega t + j \sin \omega t) \quad . \quad . \quad . \quad (5)$

The value of g can thus be calculated from (3) and (5). It may be observed that in particular, by putting $\alpha = 0$ in (4), we obtain the case of steady sinusoidal high frequency current already solved

For linear variation of current density with time, let $g = g_1 + g_2$ where g_1 is a function of r only and g_2 a function of t only.

Substituting this value of g in (1) we get

$$\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg_1}{dr} - A_1 \frac{dg_2}{dt} = 0. \quad . \quad . \quad . \quad (6)$$

This is possible when

$$\frac{d^2 g_1}{dr^2} + \frac{1}{r}\frac{dg}{dr} = 4k_1 \qquad (7),\ k_1 \text{ being an arbitrary constant}$$

$$\text{and } \frac{d\xi}{dt} = \frac{4k_1}{A_1}$$

$$\text{or } \xi = \frac{4k_1}{A} t + c_3 \qquad (8)\ c_3 \text{ being an arbitrary constant}$$

$$\text{From } (\ )\ r\frac{d^2 g}{dr^2} + \frac{dg}{dr} = 4k_1 r$$

$$\text{or } r\frac{dg_1}{dr} = 2k_1 r^2 + c \qquad c_2 \text{ being an arbitrary const}$$

$$\text{or } \frac{dg_1}{dr} = 2k_1 r + \frac{c}{r}$$

$$\text{or } g_1 = k_1 r^2 + c \log r \qquad (9)$$

Thus combining (8) and (9) we get

$$g = g_1 + \xi = k_1 r + \frac{4k_1}{A_1} t + c \log r + c_3$$

Fuller discussion of the problem will be given in later publication The author has pleasure to record his grateful thanks to Dr S S Banerjee for suggesting the above problem and helpful discussions.

Reference

(1) A G Warren *Mathematics Applied to Electrical Engineering* p 243 (Chapman and Hall Limited 1939)

PREPARATION AND STUDY OF THORIUM BORATE JELLIES

By

S P Mushran M Sc , D Phil

(Chemical Laboratory, The University Allahabad)

Received on August 12 1918

ABSTRACT

(1) Thorium borate jellies have been prepared and studied The jellies were obtained by the slow coagulation of a purified sol of thorium borate having the composition $4ThO \quad Th_3(BO_3)_4$ obtained by dispersing freshly precipitated thorium borate in excess thorium nitrate, by electrolytes like potassium chloride and potassium sulphate

(2) The sol gel transformation of thorium borate has been investigated It has been shown that the time of gelation θ is related to the concentration c of the coagulating electrolyte as $\log S = \log R + P \log c$ where R and P are constants and $S = 1/\theta$

(3) The influence of temperature on the time of setting of the jellies has been studied It is observed that the jellies set more readily at higher temperatures than at low. The jellies are not formed above 50 C

(4) The jellies are thixotropic in nature The study of their thixotropic behaviour shows that the original time of setting of the jellies is always greater than the thixotropic time of setting On repeated shakes the jellies lose their property of developing hydration and ultimately break up

(5) The influence of 20% glucose and glycerine on the time of setting of the jellies has been investigated It has been observed that glucose and glycerine exer markedly peptising influence on thorium borate sol and in their presence the original time of setting is increased

(6) It has been shown that the minimum amount of electrolyte necessary to give a jelly of the sol of thorium borate is always greater than that required to coagulate it The gelation and the coagulation points of thorium borate sol are thus two distinct points

In some of the previous publications from these laboratories[1] the conditions of formation of thorium phosphate, arsenate, molybdate and tungstate jellies have been described No attempt appears to

have been made to prepare the jellies of thorium borate. Berzelius[2] reported that boric acid precipitates white flocculent thorium borate when added to a solution of a salt of that element. Guertler[3] could not prepare thorium borate by fusing thoria with boric oxide on account of the very sparing solubility of the thoria Karl[4] has discussed the composition of the amorphous white precipitate obtained by treating an aqueous solution of thorium nitrate with a hot solution of borax and showed that the composition corresponded to thorium orthoborate, $Th_3(BO_3)_4$. It has been now observed that the white precipitate of thorium borate obtained on adding a hot concentrated solution to thorium nitrate solution, can be made to dissolve, on vigorous shaking in presence of an excess of the latter. In this way a considerable amount of thorium borate can be made to disperse in thorium nitrate. If this mixture be dialysed until nearly free from all electrolytes, a clear colourless sol of thorium borate is obtained which can be shown to be positively charged by the cataphoretic method It is easily coagulated with electrolytes like potassium chloride and potassium sulphate and when suitable concentrations of the coagulating electrolytes are used the sol sets to beautiful transparent jellies In a note Mushran[5] has briefly described the conditions of preparation of this hydrogel and in this paper the details of the preparation and various properties of the gel have been investigated.

EXPERIMENTAL

A sol of thorium borate was prepared allowing a hot 20 percent solution of borax to run slowly into 75 c.c. of 10 percent thorium nitrate solution until the precipitate of thorium borate scarcely dissolved in thorium nitrate on vigorous shaking. The mixture was purified by dialysis, for eight days, at room temperature (30°C).

COMPOSITION OF THE SOL

The amount of thorium in a known volume of the sol was estimated by the use of the reagent cupferron. (Baudisch, Chem. Ztg., 33, 1298 (1909)) The amount of borate in the combined state with thorium was found by coagulating a known amount of the sol cataphoretically, the coagulum was collected and washed and estimated for

boric acid by the usual method (Clowes and Coleman 1938 page 418). The combined thorium corresponding to this amount of borate was calculated on the assumption that the thorium borate is $Th_3(BO_3)_4$. The rest of the thorium is present as hydrated thorium oxide. From the ratio of the free to the combined thorium, the empirical formula of the sol was calculated. An analysis is presented in Table I.

TABLE I

Per litre:

Total Thorium (Th)	..	...	18.0200 g
Combined Borate (BO_3)	...	...	2.6054
Combined Thorium (Th)	...	...	7.7112
Free Thorium (Th)	...	...	10.3088
Empirical Formula	...	...	$4ThO_2.Th_3(BO_3)_4$

When this sol was coagulated with N KCl and N/5 K_2SO_4 it gave beautiful transparent jellies. The influence of the variation of the concentration of the coagulating electrolyte on the time of the setting of the gel is shown in Table II.

TABLE II

Amount of sol taken - 2 c.c. Total volume – 3 c.c. Temp – 30°C

Amount of N KCl (c.c.)	Time of setting (mins)
1·00	4
0·80	8
0·60	12
0·40	20
0·20	52

Amount of N/5 K_2SO_4 (c.c.)	Time of setting (mins)
0·28	2
0·26	4

0 24	7
0 22	10
0 20	15
0 18	20

Influence of Temperature

The influence of temperature on the time of setting of the jellies has been investigated The results are recorded in Table III

TABLE III

Volume of sol = 2 c c Total volume = 3 c c

	Time of setting (mins)				
N KCl (c c)	25	30	40	50	60
1 00	7	4	3	1	No Jelly
0 80	10	8	5	3	,,
0 60	16	12	7	4	,,
0 40	24	20	15	7	,,
0 20	65	52	42	26	,,
N/5 K_2SO_4 (c c)					
0 28	5	2	Instantaneous Loose Jelly		No Jelly
0 26	8	4	,,	,,	,,
0 24	9	7	4	1	,,
0 22	12	10	7	4	,,
0 20	17	15	12	6	,,
0 18	23	20	16	10	,,

Influence of Glucose and Glycerine

The influence of glucose and glycerine on the time of setting of the jellies have also been investigated The resultsare tabulated in Table IV

TABLE IV

Influence of Glucose 20%

Volume of sol = 2 c c Total volume = 3 c c Temp = 30 C

Glucose 20 % (c c)	Time of setting (mins)	
	0 20 c c N KCl	0 18 c c N 5 K_2SO_4
0 0	52	20
0 2	60	25
0 4	70	32
0 6	82	43
0 8	101	56

Influence of Glycerine

Volume of sol = 2 c c Total volume = 3 c c Temp = 30 C

Glycerine (c c)	Time of setting (mins)	
	0 20 c c N KCl	0 18 c c N 5 K_2SO_4
0 0	52	20
0 2	58	23
0 4	65	29
0 6	76	41
0 8	91	54

THIXOTROPIC BEHAVIOUR

It has been observed that on vigorous shaking the jellies assume a liquid form, and the viscous liquid so obtained again sets to a jelly on standing and the process could be repeated several times The jellies are therefore thixotropic in nature The thixotropic behaviour

of the jellies has been investigated The set jelly was vigorously shaken for about one minute to ensure complete transformation to the sol form, and the time it took to set again was noted The results are tabulated in Table V

TABLE V

Volume of sol = 2 c c Total volume = 3 c c Temp = 30°C

	Time of setting (mins)	
	0 20 c c N KCl	0 18 c c N 5 K_2SO_4
Original setting	52	20
After 1st shake	34	16
,, 2nd ,,	25	14
,, 3rd ,,	20	6
,, 4th ,,	12	2
,, 5th ,,	5	Breaks
,, 6th ,,	Breaks	Breaks

Relation between the Coagulation and the Gelation Points

The relation between the coagulation and the gelation points of the positively charged thorium borate sol has also been investigated Different amount of sols were mixed with 0 20c c *N* KCl and 0 18 c c *N* K_2SO_4 solutions, the total volume was kept 3 c c in each case, and the minimum amounts of electrolytes necessary to coagulate the sol and to give the jelly in 30 minutes were recorded The results are tabulated in Table VI

TABLE VI

Electrolyte N KCl

Volume of sol (c c)	Gelation Point (c c)	Coagulation Point (c c)
1 0	0 18	0 10
1 5	0 24	0 14
2 0	0 30	0 18
2 5	0 38	0 25

	Electrolyte N/5 K_2SO_4	
1 0	0 06	0 04
1 5	1 12	0 07
2 0	0 16	0 10
2 6	0 21	0 15

Discussion

According to Karl (loc cit) when a hot concentrated solution of borax is added to thorium nitrate solution a white precipitate of thorium orthoborate is obtained according to the following equation

$$3Th(NO_3)_4+Na_2B_4O_7+5H_2O=Th_3(BO_3)_4+2NaNO_3+10HNO_3$$

The insoluble thorium borate in presence of an excess of thorium nitrate gets peptised by the adsorption of thorium, hydrogen and other positively charged ions and a positively charged sol of thorium borate is obtained The sol investigated in this paper has the composition $4ThO_2.\ Th_3\ (BO_3)_4$, showing that it contains an appreciable amount of thorium borate If this sol without dialysis is coagulated with strong concentrations of coagulating electrolytes like potassium chloride or potassium sulphate, the coagulum obtained is a white opaque heavy mass which on allowing to stand settles down as a precipitate However if the sol is purified by dialysis for a few days and then coagulated by KCl or K_2SO_4 the coagulum obtained is gelatinous and with suitable concentrations of the coagulating electrolytes gives rise to clear, transparent and stable jellies

In a paper Dube and Prakash[6] have studied the influence of the concentration of various coagulating electrolytes on the time of setting of various inorganic jellies According to them the time of setting θ is related to the concentration 'c' of the electrolyte as $\log S=\log R+P \log c$ where R and P are constants and $S=1/\theta$ It is evident that if the kinetics of the sol-gel transformation of thorium borate is represented by the above expression a straight line should be obtained on plotting the logarithm of concentration against the logarithm of the inverse of the time of setting of the gels On plotting $\log S$ against $\log c$ from

the results recorded in Table I it is observed that straight lines are obtained. The results in general therefore follow the expression given by Dube and Prakash

The influence of temperature on the time of setting of thorium borate jellies has been investigated A perusal of Table III shows that the jellies set more readily at higher temperatures than at low The jellies are not formed above 50° In a paper Prakash and Dhar[7] have studied the influence of temperature on the coagulation of several sols and have shown that smaller quantities of electrolytes are required to coagulate at 60° than the amounts required for coagulation at 30° On the basis of the above it is highly probable that as the temperature is raised the rate of coagulation and consequently the hydration of thorium borate sol is more rapidly developed and the jellies are more readily obtained Also at higher temperatures thorium borate is partly hydrolysed to thorium hydroxide which has a gteat tendency to develop hydration and hence the setting time decreases with the increase of temperature

In table IV are recorded the results of the influence of 20% glucose and glycerine on the time of setting of thorium borate jellies It is easily seen that the time of setting is markedly increased by the addition of these substances to the gel forming mixtures It is well known that glucose and glycerine are strong peptising agents and it is highly probable that in their presence thorium borate is further peptised and thus the the time of setting is greatly increased

The thixotropic behaviour of thorium molybdate, phosphate and arsenate jellies have been investigated in a paper by Prakash and Biswas[8] The thorium borate jellies investigated in this paper are also thixotropic and a perusal of Table V will show that the original time of setting of the jellies are much greater than the thixotropic time of setting On shaking the structurally imbibed liquid of the jelly is set free forming a dispersion medium for the jelly forming elements and the jellies are transformed into the sol state On standing the structure is again developed and the gel is again formed. On

repeated shakes the jelly looses its property of developing hydration and ultimately breaks up

An attempt has also been made to investigate the relation between the coagulation and gelation points of the jelly forming thorium borate sol From the results recorded in Table VI it is evident that more of the electrolytes are necessary to give the jelly of the sol in 30 minutes than to coagulate it The results are in conformity with those obtained by Gessner[9], Bhatia and Ghosh[1] and Prakash[11] for various jelly forming sols It appears that there is always a fixed amount of electrolyte necessary to give a stable jelly in a definite time Any amount lesser than this leads to coagulation without allowing the coagulated particles to develop hydration and any amount greater than this gives a gelatinous precipitate

My thanks are due to Dr Satya Prakash for his very kind interest in this work

References

1 Prakash and Dhar *J Indian Chem Soc* **7** 367 (1930)
2 Berzelius *Pogg Ann* **16**,385 (1829)
3 Guertler *Z anorg Chem* **40** 232 (1904)
4 Karl *Z anorg Chem*, **68** 57 (1910)
5 Mishra *Nature* **158** 95 (1946)
6 Dube and Prakash *Z anorg Chem* **208**,163 (1932)
7 Dhar and Prakash *J Phys Chem* **34**,954 (1930)
8 Prakash and Biswas *J Indian Chem Soc* **8**,549 (1931)
9 Gessner *Koll Chem Beih* **19** 213 (1924)
10 Bhatia and Ghosh *J Indian Chem Soc* **7**,687 (1930)
11 Prakash *J Indian Chem Soc* **9** 137 (1932)

INTENSITY VARIATIONS OF RADIO SIGNALS AND THEIR BEARING ON DIVERSITY RECEPTION

By

Ram Neti Singh M Sc

University Research Scholar

Engineering College, Banaras Hindu University

(Communicated by Professor A C Banerji, F N I T N A Sc ,)

24th August 1948

1 Introduction

Appleton and Barnett (1) showed the existence of ionized layer in the upper atmosphere by their experiments on fading of radio signals as early as in 1925 Since then various investigators (2-5) became interested with the study of signal intensity received at a distance from the transmitter, particularly for the purpose of investigating the conditions of the ionosphere suitable for establishment of radio communications between two stations

In these experiments medium waves were generally employed and observations were taken mostly in the presence of ground wave In case of short waves, however, the fading of signals has been recorded outside the reach of ground wave, and the nature of variations of intensity of the received signal has been found to be rather irregular Such variations have been attributed to random scattering of signal from diffracting centres in the ionosphere by Ratcliffe and Pawsey (3) Observations on short wave signals had shown that variations of intensity were often very quick and sometimes possessing periodic characteristics Satisfactory explanations for various types of fading observed, particularly for short distance transmissions however, appear to be still very inadequate

For reasons stated above it was considered useful to make some detailed investigations of the fading of short wave signals and a few

preliminary reports on such observations have already been published from this laboratory (6,7). The present communication is intended to exhibit the occurrence of various types of fading observed for short wave transmissions on wavelengths of 19 to 41-metre-bands from Delhi and also from foreign and other Indian stations. In order to study the finer details of the intensity variations of received signals, continuous records of the observations were made on much extended time scale. The various types of fading have been conveniently divided into three main groups according to their mode of formation, namely,

(1) Random variation of peaky type,

(2) Slow and comparatively regular or quasi-periodic variations, and

(3) Regular variations of periodic nature.

The various types of fading have been accounted for by the different conditions of the ionosphere at the time of observations. It has been further shown that such experimental investigations on fading of signals are useful for the development and understanding of the principle of diversity reception of radio signals. Theoretical considerations and experimental observations show that it is possible to minimize the fading of received signals from a distant transmitter by space-diversity reception with vertically spaced aerials situated at a much smaller distance between them compared to the distance required in case of horizontally spaced aerials usually used for such reception.

2. THEORETICAL CONSIDERATIONS

It is generally assumed that the variations of intensities of radio signals at a distance from the transmitter are of random nature. Some investigators (5), however, have reported that this assumption does not hold good on many occasions particularly when the receiver is at a large distance from the transmitter This inconsistency between the observed and the theoretically assumed variations indicates that during the period of observatons there must have been occasions

when the variation of the intensity of signal was less random or it acquired some characteristic of periodic nature.

For the above considerations the observations were recorded on a much extended time scale as stated before and all the three types of fading mentioned in the previous section were obtained. These types of fading have been found to continue sometimes for a fairly long time, and also the patterns of fading have been observed changing with time.

The various types of fading and their change may be attributed to single, double or multiple spot reflections at the ionosphere. For example, the peaky random type of fading will be observed when there is only one spot reflection from the ionosphere with no other reflection either from the same or any other layer. Second type of fading namely quasiperiodic or slow random, is due to more than one spot reflection either from one layer or from two different layers in the ionosphere. Evidently in such cases the resultant intensity of the received signal at any moment will depend on the vector sum of the independent components arriving from different spots of the ionosphere. Thus at an instant when the strength of the signal due to one component tends to increase, the other component may tend to decrease and thereby the resultant intensity may remain comparatively constant. This reduces the peaky nature of the received signal and gives rise to slow random pattern. The above principle of reduction of fading is utilised in space diversity reception by using more than one aerial system as described in the subsequent section.

The third or periodic type of variation of signal intensity may be attributed to two different causes. One is due to interference fringes caused either by single and double reflections from the same layer or by two single reflections from two different layers, when one or both the layers have slow vertical movement. The other is due to magnetoionic splitting of the incident wave at the ionosphere when the electronic density in the ionospheric layer is decreased to a value corresponding to maximum usable frequency for the wave

used for transmission as suggested by Appleton and Beynon (8) Both these types of fading have been observed by us and the records of these are shown in the following section

3 EXPERIMENTAL ARRANGEMENT

A 5 valve superhet receiver was built without automatic volume control system and was employed for visual observations of the received signal intensities A sensitive and low resistance moving coil mirror galvanometer was connected in the diode circuit of the second detector of the receiver for observing the fading of received signals Usually the observations were made at interval of 5 seconds and the scale deflections could be measured up to 50 cms

In order to have a continuous record of the observations an automatic recorder was constructed The arrangement consisted of a 7-valve superhet commercial receiver, the *a v c* of which was made inoperative The rectified voltage developed across the resistance in the diode circuit of the second detector of the receiver was amplified by means of a two stage direct coupled amplifier The amplified voltage so obtained was applied to a recording galvanometer which had a writing pen attached to it The initial plate current in the galvanometer was balanced by means of an external battery of about 30 volts The writing pen moved in a vertical plane over which 4-inch wide paper for recording was run by a self-governed electric motor The vertical speed of the paper could be varied and the deflections of the recording galvanometer were calibrated for field intensities

4 OBSERVATIONS

Typical records of the three types of fading, mentioned in the previous section, are shown in figs 1 4 For convenience, the description of the diagrams is summarised in table I below In order to check the conditions for different types of fading patterns, the electronic densities in F_2—layer at the time of observations, were calculated from the ionospheric data supplied by the Research Deptartment All India Radio, Delhi, and they are included in the last column of the

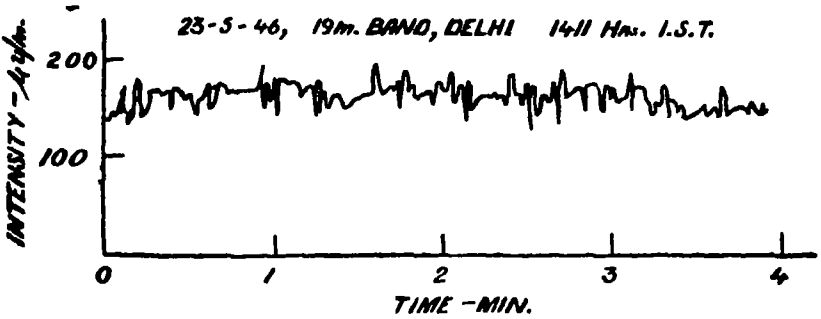


Fig. 1

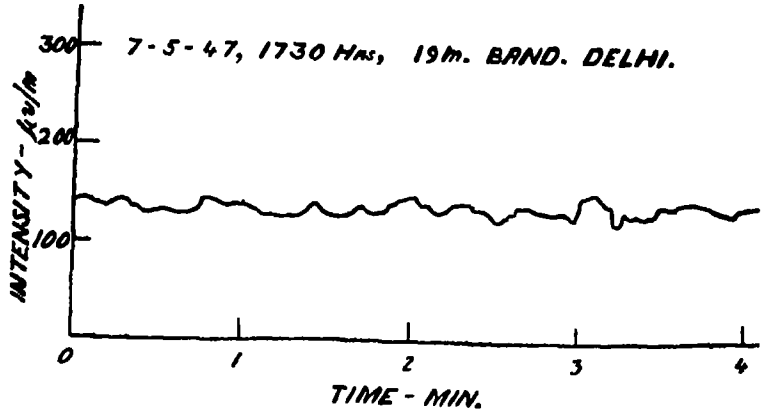


Fig. 2

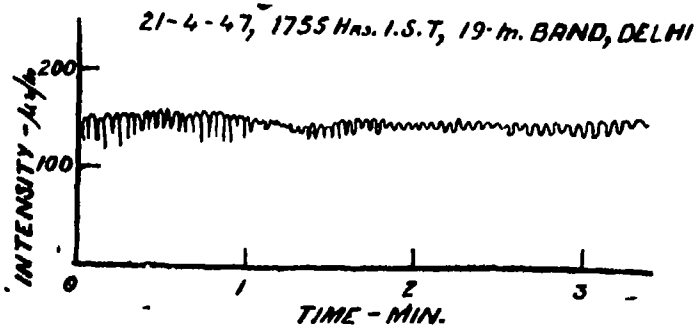


Fig. 3

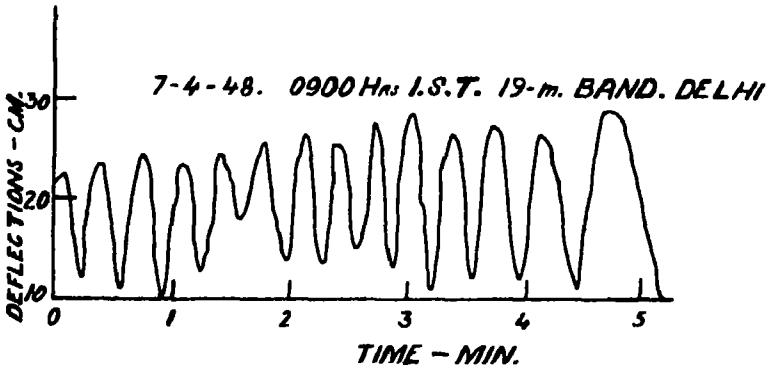


Fig. 4

table. These values may be compared with the minimum electronic densities required for single and double reflections from the F_1 layer for the distance between Banaras and Delhi (678.4 km), which were calculated and found to be 1.2×10^6 and 1.9×10^6 electrons /cc. respectively. For these calculations, thickness of the ionospheric layer and curvature of the earth have been taken into consideration.

TABLE I.

Figs.	Date.	Time in Hrs. I. S. T.	Wave band.	Type of fading.	Remarks.
1.	23-5-46	1411	19-metre.	Random.	Single reflection From F_2 (N = 1.6×10^6 electrons/cc.)
2.	7-5-47	1730	do.	Slow Random.	Double reflection From F_2 – layer [N = 2.45×10^6 elec./cc]
3.	21-4-47	1755	do.	Periodic.	Double reflection from F_2 – layer [N = 1.93×10^6 elec./cc]
4.	7-4-48	0900	do.	Smooth Periodic.	Single reflection from F_2 – [N = 1.5×10^6 elec./cc.]

It will be observed from Figs. 1 and 4 that under suitable conditions single reflections from F_2—layer may give rise to either random or smooth periodic variation of intensity of the signal. Similarly from Figs. 2 and 3 it will be seen that doubly reflected signals from F_2—layer will give rise to either slow random or periodic variations from the received signals which may be superimposed on slow random variations. There is, however, a notable difference in the periodic nature of fading between Figs. 3 and 4. The former is due to interference fringes caused by vertical movement of the layer when the electronic density is fairly high and the latter is caused by magneto-ionic splitting of the signal passing through the ionosphere with varying electronic density when it approaches the value corresponding to the maximum usable frequency for the distance between the transmitting and receiving stations. Evidently the period on the former occasion will be usually quick compared to that on the latter occasion as shown in Figs. 3 and 4 respectively.

5. Space Diversity Reception.

If there are two receiving aerials separated by a few wavelengths from each other in a horizontal plane, it is possible that they will be acted upon by reflections from two spots in the ionosphere and consequently the variations of intensity in the two aerials will be independent of each other. This principle is made use of in space diversity reception, where the outputs from two or more receivers connected to aerials which are several wavelengths apart from each other, are combined together to obtain a fairly constant strength of the signal received. It may be shown that such independent variations of the signal intensity can be obtained in two vertically-spaced aerials with much smaller separation than that required for horizontally-spaced aerials.

In order to verify the above, two vertical aerials were erected at different heights and seperated from each other by about one-third wavelength and were connected to two superheterodyne receivers of equal sensitivities and placed near each other. The receivers were connected to the aerials with transmission lines. Arrangement was

made to observe the intensity of rectified signals in the two receivers as well as their total intensities The variations of these intensities are shown in Fig 5 The dotted line represents the variations of intensity in the lower aerial denoted by G in the diagram, the dash doted line shows the variations in the upper aerial denoted by E, and the continuous line shows the resultant intensity T obtained experimentally as described above It will be observed that though there are large variations in the two aerials G and E their phases are generally opposite to each other and as such the total intensity remains nearly constant

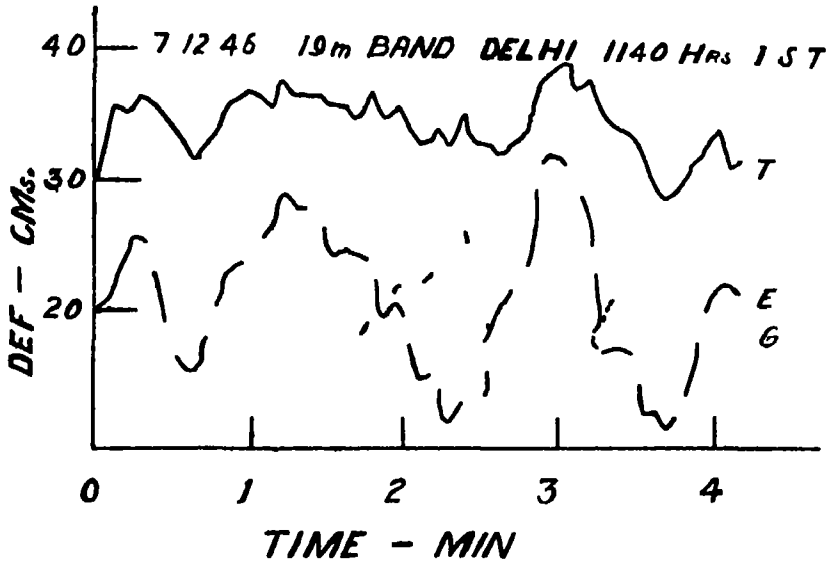


Fig 5

In order to compare similar variations of intensities in the horizonatally spaced aerials, observations were taken with one additional aerial installed at the same level as the upper aerial and situated nearly at the same distance from this, as the lower aerial This has been shown in Fig 6, where the dash dotted and continuous

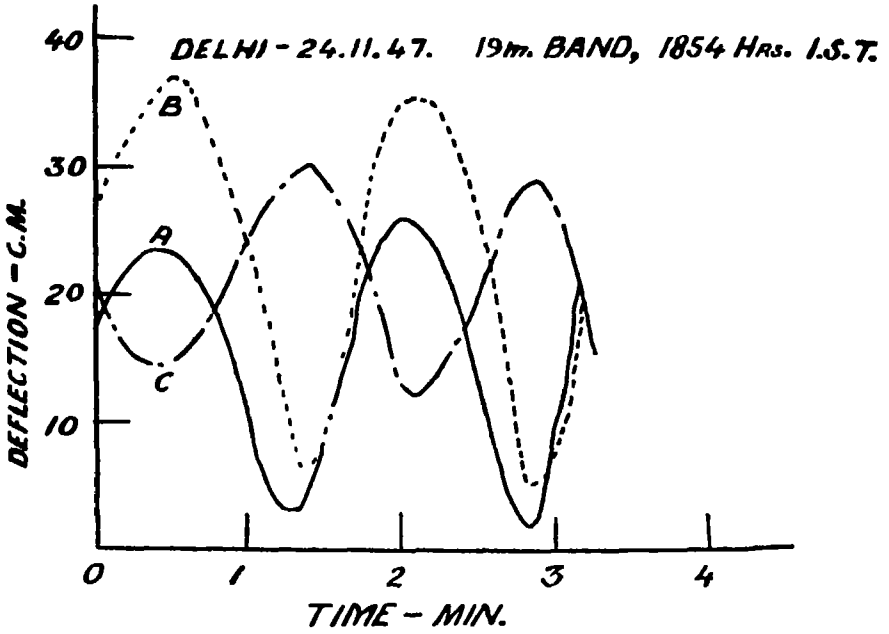


Fig. 6

curves represent the variations of intensity in the lower and upper aerials respectively denoted by *C* and *A* in the diagram, and the dotted curve shows the variations in the horizontally spaced aerial denoted by *B*. It will be observed from this figure that the variations of intensities in the horizontally spaced aerials *A* and *B* are practically in phase with each other, whereas the variations in the vertically spaced aerials *A* and *C*, are generally out of phase. Thus the resultant output from the two vertically spaced aerials will be fairly constant as compared to the combined output from the horizontally spaced aerials.

6. Summary and Conclusions.

Various types of fading of shortwave radio-signals have been observed and they have been divided into three main categories, namely (1) random, (2) slow random, and (3) periodic. Visual and automatic records of the above observations have been made and the various types of fading have been explained by assuming random scattering of radio waves from the ionosphere. The first and the

second type of fading have been attributed respectively to single-spot or double and multiple-spot reflections of radio waves from the ionosphere. The third or periodic type of fading has been found to be due to interference fringes caused by either two waves reflected from one or two layers when they possess slow vertical movement or by magneto-ionic split waves, when the electronic density in the ionosphere reaches the value corresponding to the maximum usable frequency for the distance between the transmitter and receiver. Both the above periodic types of fading have been recorded and the conditions of their formation have been verified by the ionospheric data obtained at the time of observations of the fading patterns. Utility of these observations in space-diversity reception has deen indicated. A part of this paper was read and discussed in the Indian Science Congress held in Delhi, in January 1947.

In conclusion, the author has great pleasure in recording his thanks to the Research Deparment, All India Radio, Delhi, for supplying the ionospheric data and to Dr. S. S. Banarjee for his guidance, criticisms and suggestions during the course of the present investigations. His thanks are also due to Prof. G. C. Mukerjee and principal M. M. Sengupta for their helpful interest in the work.

Section of Communication
Engineering & Applied Physics
Banaras Hindu University,
Banaras.
7. 8. 48

References.

1. E. V. Appleton and M. A. F. Barnett, *Nature*, 115, 333, 1925.
2. E. V. Appleton, *Journ. Inst. Elec. Eng.*, 66, 872, 1928.
3. J. A. Ratcliffe and J. L. Pawsey, *Proc. Camb. Phil. Soc.*, 29, 301, 1933
4. S. R. Khastgir and A. K. Ray, *Ind. Jour. Phy.* 14, 283. 1940.
5. M. M. Sengupta and S. K. Dutt, *Ind. Jour. Phy.* 15, 447, 1941.
6. S. S. Benerjee and G. C. Mukerjee, *Science and culture.* 11, 571 1946.
7. S. S. Banerjee and G. C. Mukerjee, *Nature.* 155. 15, 1946.
8. E. V. Appleton and W. J. G. Beynon, *Proc. Phy. Soc.* 59, 58, 1947.

STUDIES IN THE NATURE OF HYDRATED FERRIC OXIDE PART II ADSORPTION OF VARIOUS IONS BY THE HYDRATED OXIDE IN ACIDIC, ALKALINE AND NEUTRAL MEDIA

By

ARUN K. DEY

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SAUGAR

AND

SATYESHWAR GHOSH

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALLAHABAD

Read at the meeting on 3rd May 1948

ABSTRACT

The adsorption of the cations sodium and copper and that of the anions chloride, oxalate and ferrocyanide by hydrated ferric oxide has been studied quantitatively. It has been observed that the adsorption of the cations is enhanced when the medium is alkaline, whereas the adsorption is minimum in an acidic medium. On the other hand, the adsorption of anions is pronounced in acidic medium, and the adsorption decreases with the fall in hydrogen ion concentration of the medium. The results have been discussed and the mechanism has been explained on the basis of proton donating and proton accepting capacity of the hydroxide under different conditions.

In Part I of the series[1] we have described our results on the precipitation of hydrated ferric oxide under different conditions of temperature and with varying concentrations of the reactants ferric chloride and sodium hydroxide solutions. It was observed that the precipitation of hydrated ferric oxide is complete when the amount of sodium hydroxide is about 7 per cent less than the theoretical amount needed. A similar phenomenon has been recorded by Britton in the case of several hydroxides, where he observes that in all the cases of the metal hydroxides investigated, a lesser quantity of hydroxyl ions are able to bring about the separation of metals as insoluble hydrated oxides. In the case of cupric hydroxide the amount of

alkali required to precipitate copper as hydroxide is about 10 per cent less than the theoretical quantity as reported in an earlier communication[3]. This phenomenon has been explained by us on the basis of hydrolytic adsorption of the acid radical, resulting in the liberation of an equivalent quantity of hydroxyl ions, which cause the precipitation of the hydrated oxide.

In the course of our studies on the adsorption by amphoteric oxides, like stannic hydroxide, as we have observed in an earlier paper[4], the amount of adsorption of ions by an amphoteric oxide is intimately connected with the hydrogen ion concentration of the medium in which the hydrated oxide is suspended. Thus, in the case of hydrated stannic oxide, in the presence of minute quantities of alkali, the adsorption of basic groups like silver ions or the dye methylene blue was pronounced, while in the presence of an acid, the adsorption of ferrocyanide or that of the dye Orange II was prominent.

Since ferric oxide, by virtue of its being able to form ferrites, is of an amphoteric nature, we have in this paper studied quantitatively the adsorption of the basic ions sodium and copper —and that of acid ions -chloride, ferrocyanide and oxalate - in acidic, neutral and alkaline media.

EXPERIMENTAL

Hydrated ferric oxide was prepared by the interaction of equivalent amounts of ferric chloride and sodium hydroxide in aqueous solutions, The reagents were tested for their purity and the sodium hydroxide solution was free from carbonate. The solution of ferric chloride employed was estimated both for iron and chlorine and was found to contain these ions in equivalent quantities. For making the solutions, water free from carbon dioxide was used. The precipitate of ferric hydroxide was washed free from a majority of chlorine ions and finally dialysed till chloride ions were completely removed. The precipitate of the hydrated oxide was then shaken with water in a Jena bottle till a homogeneous suspension was obtained. For all adsorption experiments the freshly prepared suspension of ferric hydroxide containing 0.1358 gram of Fe_2O_3 per 25 c. c. was employed.

For determining the amount of a particular ion adsorbed by the oxide, 25 c. c. of the suspension was taken in several 100 c. c. graduated flasks, and measured quantities of the solutions of electrolytes were added. The medium was made acidic or alkaline by adding 1 c. c. of M/100 solutions of either sulphuric acid or sodium hydroxide before raising the volume of the mixture to 100 c. c. The heterogeneous mixture was well shaken and kept immersed in a thermostat at 30° for half an hour. When the hydrated oxide had settled, a measured volume of the clear supernatant liquid was pipetted out and the ion available in the solution determined. Knowing the total amount of the ion present in 100 c. c. of the mixture, the amount of ion associated with the precipitate was found by difference. In the tables below, the ions adsorbed by 0 3158 gram of ferric oxide are expressed in milligram ions in a total volume of 100 c. c. of the mixture.

Adsorption of Sodium ions from sodium chloride solution

Sodium in the supernatant liquid was determined by evaporating a measured volume of the liquid to dryness with a drop of hydrochloric acid, heating the residue to constant weight and finally weighing as sodium chloride. The results are given in the following table.

TABLE I

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
20.00	19.56	0.44	19.26	0.74	19 14	0.81
15.00	14 82	0.18	14.34	0.66	14.23	0 77
10.00	9.96	0.04	9.43	0.57	9 33	0.67
5.00	5.00	–	4.56	0.44	4.47	0.53

Adsorption of cupric ions from cupric sulphate solution

Copper was estimated in a measured volume of the supernatant liquid by the iodometric method. Since in an alkaline medium there are chances of the removal of copper as hydroxide, the adsorption was measured in acidic and neutral media only. In Table II the experimental results are presented.

TABLE II

Initial Concentration	Acidic Medium: Final Concentration	Acidic Medium: Adsorption	Neutral Medium: Final Concentration	Neutral Medium: Adsorption
40.00	38.05	1.95	38.05	1.95
30.00	28.35	1.65	28.35	1.65
20.00	18.65	1.35	18.65	1.35
10.00	8.95	1.05	8.95	1.05

Adsorption of chlorine ions from sodium chloride solution

In a measured volume of the supernatant liquid chloride was estimated by titration using standard potassium thiocyanate solution, and ferric alum as indicator. The adsorption of chlorine ions under different conditions are recorded below.

TABLE III

Initial Concentration	Acidic Medium: Final Concentration	Acidic Medium: Adsorption	Neutral Medium: Final Concentration	Neutral Medium: Adsorption	Alkaline Medium: Final Concentration	Alkaline Medium: Adsorption
20.00	19.37	0.63	19.38	0.62	19.43	0.57
15.00	14.56	0.44	14.56	0.44	14.60	0.40
10.00	9.75	0.25	9.76	0.25	9.80	0.20
5.00	4.89	0.11	4.90	0.10	5.00	—

Adsorption of ferrocyanide ions from potasium ferrocyanide solution

Ferrocyanide was estimated by titration against standard potassium permanganate solution. The change of colour from green to golden yellow marked the end point of the titration. The adsorption of ferrocyanide ions are shown in Table IV.

TABLE IV

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
43.6	42.0	1.6	42.0	1.6	42.5	1.1
32.7	31.5	1.2	31.5	1.2	32.0	0.7
21.8	21.0	0.8	21.0	0.8	21.5	0.3
10.9	10.5	0.4	10.5	0.4	10.9	–

Adsorption of oxalate ions from potassium oxalate solution

Oxalate in the supernatant liquid was determined by titration against standard potassium permanganate solution. The amounts of oxalate ions adsorbed are presented in the following table.

TABLE V

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
80.0	77.5	2.5	78.0	2.0	78.5	1.5
60.0	58.0	2.0	58.5	1.5	59.0	1.0
40.0	38.5	1.5	39.0	1.0	39.5	0.5
20.0	19.0	1.0	19.5	0.5	20.0	–

DISCUSSION

On a perusal of the experimental results presented in tables I to V, it is evident that the extent of adsorption of various ions investigated here, lie in the following order when the adsorption measurements are carried out in an acidic medium:

$$Cu^{++} > C_2O_4^{--} > Fe(CN)_6^{----} > Cl^- > Na^+$$

The order changes in a neutral medium to the following:

$$Cu^{++} > Fe(CN)_6^{----} > Na^+ > Cl^- > C_2O_4^{--}$$

When the medium was made alkaline the order totally changed to:

$$Na^+ \quad Cl^- \quad Fe(CN)_6^{----} \quad C_2O_4^{--}$$

It may be noted that the change of media from acidic to alkaline totally reverses the order in which the metallic or acidic ions are adsorbed. In an acidic medium, the adsorption of sodium was only 0.44 mgm ions when the initial concentration was 20.00 mgm ions, whereas in an alkaline medium the adsorption increased to 0.86 mgm ions. On the other hand, the acid radicals are preferentially adsorbed in an acidic medium as found from tables III to V.

In part I of the series, we suggested the following scheme to account for the chemical behaviour of ferric hydroxide:

$$Fe(OH)_3 = Fe(OH)_2^+ + OH^- \quad \text{.....(i)}$$

$$2Fe(OH)_2^+ = Fe_2O_3 + 2H^+ + H_2O \quad \text{.....(ii)}$$

$$H^+ + OH^- = H_2O \quad \text{.....(iii)}$$

In equation (i) the precipitated ferric hydroxide liberates OH^- ions and is, therefore, capable of behaving as a proton acceptor and accounts for the basic nature of ferric hydroxide. Thus, if an excess of hydrogen ions is maintained in the system, the reaction will proceed from left to right and the basic character of the oxide will be more pronounced. Under these circumstances, acid groups like chloride, ferrocyanide and oxalate will naturally be preferentially adsorbed.

Equation (ii) illustrates the acidic behaviour as shown by the liberation of a proton by $Fe(OH)_2$. In this case the acid properties of the oxide are prominent, since it behaves as a proton donator. This

is substantiated by the observation that sodium ions are preferentially adsorbed in an alkaline medium and that the adsorption of sodium diminishes as the acidity of the medium increases

Therefore, it is evident that since the acid or basic properties of an oxide is dependent on its proton donating or proton accepting capacity which may be regulated by the hydrogen ion concentration of the medium the adsorption of cations or anions would naturally vary with the conditions of hydrogen ions of the medium in which the hydrated oxide is suspended

Further work in this direction it is hoped, will be able to substantiate the view developed in the present series of papers on hydroxides

Refs

1 Dey and Ghosh *J Indian Chem S* 1949, 26
2 Britton *J Chem Soc* 1925, 2709
3 Dey and Ghosh *J India Chem Soc* 1947 24 181
4. Dey and Ghosh *Proc Nat Acad Sci India* 1946, 15A 143

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1948

PART IV] SECTION A [VOL. 17

ON THE RATIONAL SOLUTION OF THE DIOPHANTINE EQUATION

$$a(x^{m-1}-1)-b(y^{n-1}-1)=z^{p-1}$$

By

D. P. BANERJEE

(Communicated by Professor A. C. Banerji, Head of the Department of Mathematics, Allahabad University, Allahabad)

Received on 24-3-49

Tchacaloff and Karamicoloff[1] have considered the solution of of the Diophantine equation $Ax^m+By^n=z^p$ where $(m, n)=1=m, p=(n, p)$. Siegal[2] has proved the possibility of the solution of the Diophantine equation $ax^n-by^n=C$.

The Diophantine equation $a(x^{m-1}-1)-b(y^{n-1}-1)=z^{p-1}$ is required in solving many problems in Theory of numbers. Here I shall prove the possibility of the existence of rational solution.

The following theorem is required:-

Theorem 1. If m, n, p are Coprime integers and $M=(m-1)(n-1)(p-1)$ and $M_1=\frac{M}{m-1}$, $M_2=\frac{M}{n-1}$, $M_3=\frac{M}{p-1}$ and $\alpha_1, \alpha_2, \alpha_3$ be a set of integers such that $1+\alpha_r M_r\equiv 0 \pmod{mr-1}$ $m_r=m, n, p$, then the rational solution of the Diophantine equation $Ax_1^{m-1}-Bx_2^{n-1}=x_3^{p-1}$ for which $x_1, x_2, x_3\neq 0$

will be given by

$$x_1=X_1^{\frac{1+\alpha_1 M_1}{m-1}} X_2^{\frac{\alpha_2 M_2}{m-1}} X_3^{\frac{\alpha_3 M_3}{m-1}}$$

$$x_2=X_1^{\frac{\alpha_1 m_1}{n-1}} X_2^{\frac{1+\alpha_2 M_2}{n-1}} X_3^{\frac{\alpha_3 M_3}{n-1}}$$

$$x_3=X_1^{\frac{\alpha_1 M_1}{p-1}} X_2^{\frac{\alpha_2 M_2}{p-1}} X_3^{\frac{1+\alpha_3 M_3}{p-1}}$$

where $AX_1 - BX_2 = X_3$.

If α_1 be the value of α satisfying the equation $1+\alpha_1 M_1 \equiv 0$ (*mod* $m-1$) then $1+\alpha_1 M_1+\lambda (m-1) M_1 \equiv 0$ (*mod* $m-1$). Hence the equation $1+\alpha_1 M_1 \equiv 0$ (*mod* m_1-1) is satisfied in an infinity of ways.

It is evident that we can always find integers X_1, X_2, X_3 satisfying the equation $A X_1 - B X_2 - X_3$ when A and B are rational.

If X_1, X_2, X_3 satisfy the equation $AX_1 - BX_2 \; X_3$ then $X_1^1 = X_1+\lambda B$, $\times_2^1 = X_2 \times \lambda A$ will also satisfy the equation. Hence the equation $A X_1 - BX_2 - X_3$ may be solved in infinite ways.

Hence the Diophantine equation $A X_1^{m-1} BX_2^{n-1} = X_3^{p-1}$ may be solved in an infinite ways.

Since $1+M_r \alpha_r \equiv 0$ (*mod* $mr-1$) and $M_1 \equiv 0$ (*mod* $p-1, n-1$); $M_2 \equiv 0$ (*mod* $m-1, p-1$); $M_3 \equiv 0$ (*mod* $m-1, n-1$) and X_1, X_2, X_3 are integers then x_1, x_2, x_3 will also be integers.

Theorem 2. The Diophantine equation $a(x^{m-1}-1) - b(y^{n-1}-1) - z^{p-1}$ may be solved in integers in an infinite ways.

Let $x^{m-1} - \lambda x_1^{m-1} = 1$ *and* $y^{n-1} - \mu r x_2^{n-1}$, $x_3 = 2$, $a^1 = \lambda a$, $b^1 = \mu l$.

Then $a^1 x_1^{m-1} - b^1 x_2^{n-1} = x_3^{p-1}$ . . . . . (1)

By theorem 1 the equation (1) may be solution integers in an infinite ways.

Again [31] the equation $x^{m-1} - \lambda x_1^{m-1} = 1$ has at most one solution in integers x, y when λ exceeds certain limit which depends on m when $m > C$.

Since we have infinite number of integral values of x_1 we have infinite number of integral values of x satisfying the equation $x^{m-1} - \lambda x_1^{m-1} = 1$. similarly for

Hence the equation $a(x^{m-1}-1) - b(y^{n-1}-1) = z^{p-1}$ may be solved in an infinite ways where m, n, p are relatively prime.

Reference.

1. Tchacaloff and Karamicoloff (1940) Comptes Rendus (Paris) p. 210
2. Siegel (1930) *Berliner Sitzungsberichte* pp. 1-70
3. Siegel. l.c.

NEW LINES IN CARBON SPECTRUM

By

A S Varma M Sc, Ph D.

Physics Department Lucknow University Lucknow

(Received on February 28, 1948)

(Communicated by Prof D B Deodhar Lucknow University Lucknow.)

ABSTRACT

The emission spectra of iron and pure samples of carbon were photographed on a Hilger Medium size Quartz Spectrograph E 3 in the region of 2 100 to 7 000 A U by arcs running on 220 volt D C and on alternating current lamps The lines in the iron spectrogram were identified and the relative positions of the carbon lines were measured by Hilger's Comparator and their wave lengths were calculated by applying Hartmann's Interpolation formula The lines due to impurities present in carbon specimens were eliminated, but in addition to the published carbon lines there was a positive indication of the presence of a fairly large number of new lines of varying intensity which are attributed to carbon

Introduction

Much work has been published in the past years on the analysis of line and band spectra of carbon in the ultra-violet and the extreme ultra violet regions by Fowler and Selwyne (1928) and Johnson (1925)

In the course of the spectroscopic investigations on some compounds with the help of the carbon arc it was noticed that there were some new lines attributable to carbon, and it was thought desirable to make an independent observation on the carbon arc to settle this point A carbon arc of spectroscopically pure specimens of carbon rods was set up for this purpose and spectrograms were photographed in the region of 2,100 to 7,000 A U

The observations were repeated a number of times and it was discovered that new lines existed on all the plates These lines do not seem to have been recorded by previous workers

EXPERIMENTAL

The Hilger medium size quartz spectrograph was used to photograph the iron and carbon arcs in juxtaposition with two consecutive holes of Hartmann's diaphragm The essential feature of this spectrograph is the Cornu Prism which is composed of two 30° prisms of quartz of opposite rotatory power-one dextro and the other lævo rotatory prisms in optical contact so as to cancel the optical rotations

Ilford Hypersensitive Panchromatic Plates H P 3 were exposed to photograph the emission spectra of the arcs run on 220 volts D C carrying 3 amps. current These plates were exposed and developed in absolute darkness and the spectrogram was photographed in the region extending from 2,100 to 7,000 A U

The lines of the iron spectrogram were identified and compared with the standard spectrograms published by Hilgers and the positions of the carbon lines were measured with reference to the iron lines of known wavelengths by means of the Hilger measuring micrometer L 13 and their wave-lengths were calculated by appyling Hartmann's formula which is fairly accurate over short ranges of wave-lengths

The Hartmann's interpolation formula gives

$$\lambda = \lambda_0 + \frac{C}{\eta - \eta_0}$$

where

λ is the wave-length of the line in question

λ_0, C, η_0 are constants

and η, the position of the unknown line on the micrometer scale

Measuring the distances of three known lines of Fe-spectrum and substituting in the above formula provides a set of simultaneous equations from which all the three unknown constants can be easily evaluated

Knowing all these constants and measuring the distance of the unknown carbon line with reference to the identified iron line the wave-length of the unknown line can be calculated

In this way the wave-lengths of a large number of carbon lines have been measured.

OBSERVATIONS

The carbon electrodes used for the arc spectrum were supplied by Adam Hilger Ltd London

The report accompanying these carbon electrodes which were prepared under extraordinary special conditions with a view to obtain purest possible carbon revealed the presence of the following impurities in traces on spectrographic analysis

Sodium	Na
Magnesium	Mg
Calcium	Ca
Strontium	Sr
Copper	Cu
Manganese	Mn
Aluminium	Al
Silicon	Si

According to the report, the lines due to Potassium Barium and Aluminium were not in evidence and the report provides a table of wave-lengths of th lines due to impurities present in the specimen

These lines have been completely eliminated from the spectrogram of the carbon, photographed Further all those lines found in the carbon spectrum appended in standard tables (1924) and (1932) have been taken into consideration. Apart from all these lines, there is a positive evidence of the presence of some more lines in the spectrum which have not been published by other workers

A table of the new carbon lines as observed is given below :—

S. N.	Wave-length of new Carbon lines	Frequency	Intensity
	A. U.	cm^{-1}	
1	1197.600	23823 13	3
2	3851 727	25962 39	3
3	3202 585	31224 79	2
4	3197 859	31270 93	2
5	3191.122	31336 96	1
6	3185.438	31392 87	4
7	3183 917	31407 86	5
8	3133 224	31917.10	3
9	3130.246	31947.37	2
10	3125.591	31993.96	3
11	3120.705	32044.05	2
12	3118.442	32067.3	5
13	3053.327	32751.17	4
14	3033 426	32966.03	2
15	2957.261	33815.08	1
16	2941.285	33998.75	2
17	2920 066	34245.8	2

S. N.	Wave-length of new Carbon lines	Frequency	Intensity
	A. U.	cm^{-1}	
18	2906.113	34410.2	2
19	2892 510	34572.05	1
20	2701.375	37018.18	2
21	2690 844	37163 06	2
22	2683.423	37265.84	2
23	2388 59	41865 70	4
24	2375 18	42102.08	5

The intesity of these lines has been recorded taking the intensity of the brightest line in the spectrogram as 10

Conclusions

After eliminating all lines due to impurities in the carbon specimen and the published lines of carbon there is a positive indication of the existence of 24 additional lines of carbon, the wave-lengths, frequencies and intensities of which are given in a tabular form.

A major portion of these lines are faint in intensity but their positions can be properly located with the help of the Hilgers Measuring micrometer L 13 using a suitable magnification.

These lines do not appear to belong to the bands present in the carbon spectrum

Acknowledgement

In conclusion, the author expresses his sincere and grateful thanks to Prof. D. B. Deodhar for suggesting the problem and for his valuable guidance and to the University for a research grant.

Department of Physics Lucknow University
Dated 24 th Feb 1948

References

Edern and Valenta (1924) *Atlas Typischer Spektren*

Fowler and Selwyn (1928) *Proc Roy Soc* A 120 312

Johnson (192) *Proc Roy Soc* A 108, 343

Kayser and Konen (1932) *Handbuch Der Spectroscopie* Vol 8

STRAZZERI'S FORMULA IN RECTILINEAR CONGRUENCES AND ITS APPLICATIONS

By

RAM BEHARI AND RATAN SHANKER MISHRA

DELHI UNIVERSITY

The object of this paper is to establish Strazzeri's formula * in Rectilinear Congruences by tensor methods and to obtain from it or directly various forms for sin θ where θ is the angle which a ray of the congruence makes with the normal to the surface of reference at its point of intersection with the surface.

1. Let a Rectilinear Congruence be defined by the co-ordinates $x^i = x^i(u^1, u^2)$, $i = 1, 2, 3$ of a point M on the surface of reference S and by the direction cosines $\lambda^i = \lambda^i(u^1, u^2)$, $i = 1, 2, 3$ of the line passing through M.

Then
$$\lambda^i . \lambda^i = 1. \qquad \ldots \quad (1\cdot1)$$

The functions λ^i may be expressed in terms of the direction numbers $x^i_{,\alpha}$ $(\alpha = 1, 2)$ of the tangents to the co-ordinate curves on the surface through M, and the direction cosines X^i of the normal to the surface at M. Thus
$$\lambda^i = p^\alpha x^i_{,\alpha} + qX^i \qquad \ldots \quad (1\cdot2)$$

where p^α are the contravariant components of a vector in the surface at M, 'q' is a positive scalar function and $x^i_{,\alpha}$ denotes covariant differentiation of x^i with regard to u^α based on the first fundamental tensor

* See Strazzeri, Palermo Rendiconti (1927), p. 138 ; Behari, R, Jour. Ind. Math. Soc., New Series, Vol. II (1936), pp. 163-164.

$$g_{\alpha\beta} = x^i{}_{,\alpha}\lambda^i{}_{,\beta} \qquad \ldots \quad (1\cdot3)$$

of the surface S.

From (1·2) we get, by virtue of (1·1) and (1·3),

$$\lambda^i.\lambda^i \equiv (p^\alpha x^i{}_{,\alpha} + qX^i)(p^\beta x^i{}_{,\beta} + qX^i) = p^\alpha p^\beta g_{\alpha\beta} + q^2$$

$$\text{or } 1 = p_\alpha p^\alpha + q^2 = p_\alpha p_\beta g^{\alpha\beta} + q^2 \qquad . \quad (1\cdot4)$$

If θ is the angle between the normal to 'S' at M and the line λ of the congruence at M, it follows from (1·2) that

$$\cos\theta = \lambda^i X^i - q \qquad .. \quad (1\cdot5)$$

The equation (1·4) assumes the form

$$p_\alpha p_\beta g^{\alpha\beta} = \sin^2\theta \qquad . \quad (1\cdot6)$$

Suppose the determinant $(x^i{}_{,\alpha} x^i{}_{,\beta} \lambda^i) = e_{\alpha\beta}$. (1·7)

then

$$e_{\alpha\beta} e_{\gamma\delta} = g_{\alpha\gamma} g_{\beta\delta} - g_{\alpha\delta} g_{\beta\gamma} \qquad . \quad (1\cdot8)$$

and the equation (1·6) becomes

$$p_\alpha p_\beta g_{\delta\gamma} e^{\alpha\gamma} e^{\beta\delta} = \sin^2\theta \qquad . \quad (1\cdot9)$$

2. The direction numbers $x^i{}_{,\alpha}$ $(\alpha = 1, 2)$ of the tangents to the co-ordinate curves on the surface of reference through M, may be expressed in terms of λ^i and $\lambda^i{}_{,\alpha}$ $(\alpha = 1, 2)$. Thus

$$\lambda^i{}_{,\alpha} = p_\alpha \lambda^i + q^\gamma{}_\alpha \lambda^i{}_{,\gamma} \qquad .. \quad (2\cdot1)$$

where $\lambda^i{}_{,\alpha}$ denotes covariant differentiation of λ^i with regard to u^α based on the first fundamental tensor of the spherical representation of the congruence,

$$G_{\alpha\beta} = \lambda^i{}_{,\alpha} \lambda^i{}_{,\beta} \qquad \ldots \quad (2\cdot2)$$

From (2·1)

$$\lambda^i.x^i{}_{,\alpha} = p_\alpha \qquad \ldots \quad (2\cdot3)$$

$$q^\gamma{}_\alpha = x^i{}_{,\alpha} x^i{}_{,\delta}\, g_{\beta\phi}\, E^{\gamma\beta} E^{\delta\phi} \qquad \ldots \quad (2\cdot4)$$

$$\text{where } E_{\alpha\beta} = (\lambda^i{}_{,\alpha} \lambda^i{}_{,\beta} \lambda^i), \qquad \ldots \quad (2\cdot5)$$

$$E_{\alpha\beta} E_{\gamma\delta} = G_{\alpha\gamma} G_{\beta\delta} - G_{\alpha\delta} G_{\beta\gamma} \qquad \ldots \quad (2\cdot6)$$

and $E^{\alpha\beta}$ is a tensor conjugate to $E_{\alpha\beta}$.

The first fundamental tensor of the surface of reference S is given by

$$g_{\alpha\beta} \equiv x^i{}_{,\alpha} x^i{}_{,\beta} = p_\alpha p_\beta + q_\alpha{}^\gamma q_{\gamma\beta}$$

whence, using the equations (2 4), we get using Eisenhart's notation

$$\left.\begin{aligned} E &\equiv g_{11} = p_1^2 + q_1{}^\gamma q_{\gamma 1} = p_1^2 + \frac{1}{H^2}[Ge^2 - 2Fef' + Ef'^2] \\ F &\equiv g_{12} = p_1 p_2 + q_1{}^\gamma q_{\gamma 2} = p_1 p_2 + \frac{1}{H^2}[Gef - Fff' - Feg + Egf'] \\ G &\equiv g_{22} = p_2^2 + q^\gamma{}_2 q_{\gamma 2} = p_2^2 + \frac{1}{H^2}[Gf^2 - 2Fgf + Eg^2] \end{aligned}\right\} \quad \ldots \quad (2\cdot7)$$

From these equations

$$[e_{\alpha\beta}E^{\alpha\delta}]^2 = [q^\alpha{}_\beta q^\gamma{}_\delta E_{\alpha\gamma} E^{\delta\upsilon}]^2 + [e_{\alpha\beta}E^{\alpha\delta}]^2 p_\alpha p_\beta g_{\delta\varphi} e^{\alpha\delta} e^{\beta\phi}$$

or using the equations (1·8) and (2 4) in this equation we get

$$\frac{EG-F^2}{\overline{EG-F^2}}\cos^2\theta = \frac{(eg-ff')^2}{(\overline{EG-F^2})^2} \text{ or } \frac{ds}{d\sigma}\cos\theta = \rho_1\rho_2 \quad \ldots \quad (2\ 8)$$

where ds and $d\sigma$ are the elements of areas of the surface of reference at M and the spherical representation of the congruence and ρ_1, ρ_2 are the distances to the focal points from the surface of reference.

This formula can be proved alternately by considering the determinant

$$(x^i{}_{,\alpha}\ x^i{}_{,\beta}\ \lambda^i),$$

which with the help of the equation (1·2) can be written as

$$(x^i{}_{,\alpha}\ x^i{}_{,\beta}\ \ p^\alpha x^i{}_{,\alpha} + qX^i).$$

In virtue of (1 7) this determinant becomes equal to

$$qe_{\alpha\beta}.$$

using (2·1) the determinant also beomes

$$(p_\alpha\lambda^i + q^\gamma{}_\alpha \lambda^i{}_{,\gamma}\ \ p_\beta\lambda^i + q^\delta_\beta \lambda^i{}_{,\delta}\ \ \lambda^i)$$

which using (2 5) is equal to $\quad \ldots \quad (2\cdot9)$

$$q^\gamma{}_\alpha q^\delta_\beta E_{\gamma\delta}.$$

Hence $$q e_{\alpha\beta} = q^{\gamma}{}_{\alpha} q^{\delta}{}_{\beta} E_{\gamma\delta}$$
or
$$q^{e}{}_{12} = (q^{1}{}_{1} q^{2}{}_{2} - q^{2}{}_{1} q^{1}{}_{2}) E_{12}$$
or using (2·4) we get $q \dfrac{e_{12}}{E_{12}} = \dfrac{eg - ff'}{EG - F^2}$

Hence $$\cos\theta . \frac{ds}{d\sigma} = p_1 \, p_2 .$$

3. The equation (1·9) gives an expression for $\sin^2\theta$ in terms of p_α,
$$\sin^2\theta = p_\alpha p_\beta \, g_{\delta\gamma} e^{\alpha\gamma} e^{\beta\delta} .$$

When expanded this equation becomes
$$\sin^2\theta = \frac{1}{H^2} [p_1^2 G + p_2^2 E - 2 p_1 p_2 F] \qquad \ldots \qquad (3·1)$$

Using Strazzeri's formula we now find out another expression for $\sin^2\theta$.

Covariant differentiation of λ^i in the equation (1·2) gives
$$\lambda^i{}_{,\beta} = p^\alpha x^i{}_{,\alpha\beta} + p^\alpha{}_{,\beta} x^i{}_{,\alpha} + q X^i{}_{,\beta} + X^i q_{,\beta}$$
which by means of Gauss and Weingarten equations
$$\left.\begin{aligned} x^i{}_{,\alpha\beta} &= d_{\alpha\beta} X^i \\ \text{and} \quad X^i{}_{,\beta} &= -d_{\beta\gamma} g^{\gamma\delta} x^i{}_{,\delta} \end{aligned}\right\} \qquad \ldots \qquad (3·2)$$
can be written in the form
$$\lambda^i{}_{,\beta} = \mu^\gamma_\beta x^i{}_{,\gamma} + \nu_\beta X^i$$
$$\text{where } \mu^\gamma{}_\alpha \equiv p^\gamma{}_{,\alpha} - q d_{\alpha\sigma} g^{\sigma\gamma}$$
$$\nu_\alpha \equiv q_{,\alpha} + p^\beta d_{\alpha\beta} \qquad \ldots \qquad (3·3)$$

From the equation (3·3) the first fundamental tensor for the spherical representation of the congruence is given by
$$G_{\alpha\beta} \equiv \lambda^i{}_{,\alpha} \lambda^i{}_{,\beta} = \mu^\gamma_\beta \mu^\delta_\alpha g_{\gamma\delta} + \nu_\alpha \nu_\beta \qquad \ldots \qquad (3·4)$$

Also using equation (3·3)

$$\lambda^i{}_{\beta} x^i{}_{,\alpha} = \mu^{\gamma}{}_{\beta}\, {}^{\prime}{}_{\alpha\gamma}$$

or $\mu^{\gamma}_{\beta} = g^{\gamma\alpha}\, \lambda^i{}_{\beta} x^i{}_{\alpha} = g_{\delta\varphi}\, e^{\alpha\delta}\, e^{\varphi\gamma}\, \lambda^i{}_{\beta} \cdot x^i{}_{\alpha}$

whence $\mu^1{}_1 = \dfrac{G - Ff'}{H^2}$, $\mu^2{}_1 = \dfrac{Ef - Fe}{H^2}$, $\mu^1{}_2 = \dfrac{Gf - Fg}{H^2}$ $\mu^2{}_2 = \dfrac{Eg - Ff}{H}$ ...(3·5)

Using (3 5) in (3 4) we get,

$$\left.\begin{aligned} E = G_{11} &= \nu^2{}_1 + \mu^{\gamma}{}_1\, \mu_{1\gamma} = \nu_1^2 + \frac{1}{H^2}\,[G e^2 - 2\,Fef + Ef^2] \\ F = G_{12} &= \nu_1\nu_2 + \mu^{\gamma}{}_1\, \mu_{2\gamma} = \nu_1\nu_2 + \frac{1}{H^2}[Gef - Eff - Feg + Egf] \\ G = G_{22} &= \nu_2^2 + \mu_2{}^{\gamma}\, \mu_{2\gamma} = \nu_2^2 + \frac{1}{H^2}\,[Gf^2 - 2\,Fgf + Eg^2] \end{aligned}\right\} \quad . \quad (3\ 6)$$

From these equations

$[E_{\alpha\beta}\, e^{\alpha\beta}]^2\, (1 - \nu_\alpha \nu_\beta\, G_{\gamma\delta}\, E^{\alpha\gamma} E^{\beta\delta}) = (q^{\alpha}{}_{\delta}\, q^{\delta}{}_{\gamma}\, e_{\alpha\delta}\, e_{\beta\gamma})^2\, (E_{\alpha\beta}\, e^{\alpha\beta})^2$

or $(e_{\alpha\beta}\, E^{\alpha\beta})^2\, (1 - \nu_\alpha \nu_\beta\, G_{\gamma\delta}\, E^{\alpha\gamma}\, E^{\beta\delta}) = (q^{\alpha}{}_{\beta}\, q^{\delta}{}_{\gamma}\, E_{\alpha\delta} F_{\beta\gamma})^2$

or $\dfrac{EG - F^2}{EG - F^2}(1 - \nu_\alpha \nu_\beta\, G_{\gamma\delta}\, E^{\alpha\gamma} E^{\beta\delta}) = \left(\dfrac{eg - ff'}{EG - F^2}\right)^2$

or $\left(\dfrac{ds}{d\sigma}\right)^2 (1 - \nu_\alpha \nu_\beta\, G_{\gamma\delta}\, E^{\alpha\gamma}\, E^{\beta\delta}) = (\rho\, \rho_1)^2$

$$\therefore \qquad \sin^2\theta = \nu_\alpha \nu_\beta\, G_{\gamma\delta}\, E^{\alpha\gamma}\, E^{\beta\delta} \qquad .. \quad (3\ 7)$$

in consequence of Strazzeri's formula.

When expanded this expression assumes the form

$$\sin^2\theta = \frac{\nu_1^2 G + \nu_2^2 E - 2\nu_1\nu_2 F}{H^2} \qquad ... \quad (3\ 8)$$

4 The expression (3·7) for $\sin^2\theta$ can be obtained independently of Strazzeri's formula as follows —

The functions X^i may be expressed in terms of λ^i and $\lambda^i{}_{\alpha}$

Thus $\qquad X^i = \nu^{\alpha} . \lambda^i{}_{\alpha} + q\lambda^i \qquad .. \quad (4·1)$

where ν^{α} are the contravariant components of a vector in the spherical representation of the congruence, 'q' is a positive scalar function and

$\lambda^i{}_{,\alpha}$ denotes covariant differentiation of λ^i with regard to u^α based on the first fundamental tensor

$$G_{\alpha\beta} = \lambda^i{}_{,\alpha}\, \lambda^i{}_{,\beta} \qquad .. \quad (4\cdot2)$$

of the surface S

From the equation (4·2), $\cos\theta = \lambda^i X^i = q$,

$$X^i \lambda^i{}_{,\alpha} = \nu^\beta G_{\alpha\beta} = \nu_\alpha$$

and

$$X^i X^i = \nu^\alpha \lambda^i{}_{,\alpha} + q\lambda^i)(\nu^\beta \lambda^i{}_{,\beta} + q\lambda^i)$$

or

$$1 = \nu^\alpha \nu^\beta G_{\alpha\beta} + q^2$$

or

$$\sin^2\theta = \nu_\alpha \nu^\alpha$$

or

$$\sin^2\theta = \nu_\alpha \nu_\beta G^{\alpha\beta}$$

or

$$\sin^2\theta = \nu_\alpha \nu_\beta E^{\alpha\gamma} F^{\beta\delta} G_{\gamma\delta}$$

in virtue of (2·5) and (2·6)

NOTE ON CONICS OF DOUBLE OSCULATION OF A CUBIC

By

HARIDAS BAGCHI, M. A., PH. D.,

(OFFG. HEAD OF THE DEPARTMENT OF PURE MATHEMATICS ,CALCUTTA UNIVERSITY)

Communicated by Dr. K. M. Basu, D. Sc., F. N. A. Sc., Lecturer in Applied Mathematics, University College of Science, 92 Upper Circular Road, Calcutta-9

Received on September 3, 1948.

ABSTRACT

As its title indicates, this paper (divided into four sections) is devoted to a somewhat detailed discussion of the nine systems of (∞^1 of) conics of double osculation—real or imaginary—attaching respectively to the nine points of inflexion of a given (bicursal) cubic Γ.

In Sec. I Chasles's characteristics, associated with any of the nine sets of conics have been determined, and the loci of the centres and foci have been shewn to be of respective degrees 4 and 12, whereas the envelope of the asymptotes is found to be of class 14.

Notice has been further taken of the

(i) *three* rectangular hyperbolas; (ii) *four* parabolas;

(iii) *four* pairs of lines (inflexional tangents);

and (iv) *three* 'cognate' sextactic conics,

that are included in any of the nine aforesaid systems of conic of double osculation. Incidentally, a symbolic (irrational) form of Γ in terms of three 'cognate' conics of double osculation has been established.

In Sec. II the M-invariant, the Jacobian (covariant) and a certain relevant contravariant, related to an arbitrary triad of 'cognate' conics of double osculation, have been taken into consideration. Special attention has been paid to the triad of (cognate) conics (of double osculation), qualified by a *zero* M-invariant.

In point of fact, it has been definitely proved that such a triad of conics—which includes, as a particular variety, the three 'cognate' sextactic conics—possesses a common self-conjugate triangle.

Sec. III deals principally with the canonical *homogeneous* forms, which three 'cognate' conics of double osculation—having a *null* M-invariant—assume, when their common self-conjugate triangle is chosen as the *triangle of reference*. Prominence has been given to the particular case when the three ('cognate') conics in question happen to be the three sextactic conics, included in the system.

Lastly, Sec. IV begins with a lemma, touching on the *infinitude* of 'equi-anharmonic' cubics, 'each of which counts, among its aggregate of polar conics', three *assigned* conics, endowed with a common self-conjugate triangle. The lemma has been finally applied to the investigation of the series of 'equi-anharmonic' cubics, that have for their common polar conics, an assigned triad of 'cognate' conics of double osculation,—which may or may not be sextactic conics,—related to a given (bicursal) cubic and qualified by a *zero* M-invariant.

INTRODUCTION

The present paper, as its name implies, is devoted to a discussion on the nine systems of conics of double osculation (real or imaginary), which a bicursal cubic possesses under normal circumstances. As is well-known, (non-degenerate) plane cubics are classified as *bicursal* or *unicursal*, according as their *deficiency* or *genus* is 1 or 0. Little or no notice has been taken in this paper of the comparatively simple theory of *unicursal* cubics, considering that they are derivable from ordinary conics by the process of "quadric inversion" (i. e., circular inversion combined with projection). Of course, most of the properties of *bicursal* cubics, when *properly* modified, hold also for *unicursal* varieties.

As regards the *special* use of the term *osculation* in this paper, a few words of explanation are called for. It is common knowledge that, whilst the 'osculating conic' of a curve Γ at a point P is generally defined as the conic, having five-pointic contact with Γ near P, two arbitrary curves Γ and Γ' are, generally speaking, said to '*osculate*' each other at a point P, provided they have only *three-pointic* (and *not* five-pointic) contact with each other near P. In the present context, by a '*conic of double osculation*' of a cubic Γ is meant a conic, having *three pointic* contacts with Γ at *two* points, which are usually *distinct* but may in special cases coincide.

As a matter of convenience, the paper has been divided into four sections. Section I treats of certain characteristic properties of any one of the *nine* systems of ∞^1 conics of double osculation, attaching respectively to the *nine* points of inflexion of the cubic Γ. The infinitude of conics of any of the *nine* systems—spoken of as 'cognate' to one another—contains, among others, three *sextactic* conics of Γ. Then Sec. II deals with the M-invariant, the Jacobian covariant and cubic contravariant, associated with an *arbitrary triad* of 'cognate' conics of double osculation and rightly lays great stress on a *specialised* triad of such conics, *having a zero M-invariant*; the intrinsic importance of the last-named category of triads (of conics of double osculation) lies in the fact that it includes, within its fold, the triad of '*sextactic*' conics. Thirdly Sec. III disposes of the *canonical* (homogeneous) forms of a triad of '*cognate*' conics (of double osculation)—belonging to any one of the *nine* systems—having a zero M-invariant. Finally Sec. IV begins with a digression on an arbitrary triad of conics, having a common self-conjugate triangle, and ends with an application to the special triads of conics of double osculation (of a cubic), having a *zero* M-invariant.

I beg leave to add that, although the subject-matter of this paper is classical in origin and there are occasions on which I have felt constrained to touch on *known* results, still I honestly believe that this paper embodies a very decent amount of original contributions to the subject. Even in the disposal of known results, there is, I believe, some *novelty* in the mode of treatment.

SECTION I

(General properties of systems of conics of double osculation.)

Art. 1.—We know from the Theory of Higher Plane Curves

(i) that if a conic has three-pointic contacts with a given cubic Γ (bicursal or unicursal) at two points P, Q, the chord PQ must cut Γ at a point of inflexion I;

and (ii) that, conversely, if an arbitrary transversal IPQ be drawn through a point of inflexion I of the cubic Γ, then a uniquely determinate conic can be described so as to have three-pointic contacts with Γ at P, Q.

Thus, intimately related to a point of inflexion I of a cubic Γ, there exists a family of ∞^1 conics of double osculation, whose chords of (double) osculation form a *pencil* through I. If, then, Γ be supposed to be a *bicursal* cubic of the most unrestricted type, it must have *nine* sets of ∞^1 conics of double osculation, attaching respectively to the *nine* points of inflexion (real or imaginary). For felicity of expression, we shall use the adjunct "cognate", in connection with two or more conics (of double osculation), to signify that the conics in question belong to the *same* family, *i.e.*, that their associated chords of double osculation pass through the *same* point of inflexion of the cubic. In other words, two conics of double osculation (of Γ) will be termed "cognate" or "non-cognate", according as their related chords (of double osculation) do or do not pass through the *same* point of inflexion. Adopting this nomenclature, we can simply assert that a bicursal cubic admits, in general, of nine distinct families of *cognate* conics of double osculation. The main purpose of this paper is to make a systematical study of the afore-mentioned families of conics. Our object will be realised if we confine our attention to *only one* of the *nine* systems of conics (of double osculation); for the intrinsic properties, shewn to hold for *any one* of these systems, must, from considerations of symmetry, hold also for each of the *remaining eight* systems.

In the analytic investigation to be initiated in the next article we shall find it to our convenience to approach the subject in an *indirect* manner.

Art. 2.—We shall first make use of a lemma, (the truth of which is intuitively evident) viz.,

If P, Q be the two points (real or imaginary), where a *given* conic S is met by a *given* right line u, the *most general* equation of a cubic, having three-pointic contacts with S at each of points P, Q is representable in the form :

$$S.\,v = u^3, \qquad \ldots \quad (\mathrm{I})$$

where v is an *arbitrary* right line, involving necessarily *three* arbitrary (or disposable) constants.

A cursory glance at (I) suggests that the chord of double osculation, viz., u cuts Γ at an inflexion, the tangent at which is v,—a fact otherwise obvious on *a priori* grounds. We may now look at the matter from a different perspective, and affirm that, if the cubic be *given* in the first instance and S be any of the infinitude of conics of double osculation, the equation of Γ must be of the symbolic form (I), where, of course, u, v are two right lines, of which the former is the chord of osculation, and the latter is the tangent (to Γ) at the related point of inflexion. If, as a measure of expediency, this point of inflexion be taken as the origin O of Cartesian coordinates (in general, oblique), and the lines

$$u = 0 \text{ and } v = 0$$

be taken respectively as the coordinate axes

$$x = 0 \text{ and } y = 0,$$

the Cartesian equation of the original bicursal cubic Γ may be thrown into the form

$$S.\,y = x^3, \qquad \ldots \quad (\mathrm{II})$$

where the conic, viz.,

$$S \equiv ax^2+2hxy+by^2+2gx+2fy+c=0 \quad . \quad . \quad . \quad (1)$$

osculates Γ at its two points of intersection with the axis $x=0$. Needless to say, the axis $y=0$ is the tangent to Γ at the point of inflexion O.

The equation (II) being equivalent to

$$(S+3\lambda x^2+3\lambda^2xy+\lambda^3y^2)\ y=(x+\lambda y)^3, \quad . \quad . \quad . \quad (\text{III})$$

(where λ is an *arbitrary* parameter), we readily recognise that the *general* equation of the family of ∞^1 cognate conics of double osculation (including the first conic S as a particular member) is

$$\left.\begin{array}{l} S+3\lambda x^2+3\lambda^2xy+\lambda^3y^2=0, \\ \text{i.e., } (a+3\lambda)x^2+2(h+\tfrac{3}{2}\lambda^2)xy+(b+\lambda^3)y^2+2gx+2fy+c=0. \end{array}\right\} \quad . \quad . \quad . \quad (2)$$

It goes without saying that the pencil of corresponding chords of double osculation,—passing, of course, through the related point of inflexion O—is denoted by

$$x+\lambda y=0, \quad . \quad . \quad (3)$$

where λ is, as before, a variable parameter.

It is clear on all hands that, by choosing the parameter λ in diverse ways, one can easily deduce, from (2), the equations of

(i) the *three* sextactic conics,
(ii) the *four* parabolas,
(iii) the *three* rectangular hyperbolas,
and (iv) the *four* pairs of right lines,

that are included in the family of conics of double osculation, appertaining to the point of inflexion O. Judging from elementary considerations, one can readily perceive that, unless the cubic Γ is *specialised* to a certain extent, the family will *not* include even a single circle.

The four cases (i), (ii), (iii) and (iv) will now be dealt with serially.

Case i. Observing that (2) will be a sextactic conic of Γ, if it touches the chord of (double) osculation viz. (3), we promptly realise that the *three* sextactic conics*, belonging to the system (2), are represented by the Cartesian equation

$$(a+3\lambda_r)\,x^2+2\,(h+\tfrac{3}{2}\lambda_r^2)\,xy+\,(b+\lambda_r^3)\,y^2+2gx+2fy+c=0, \qquad \text{(IV)}$$

and that the three associated sextactic points are

$$\left(\frac{c\lambda_r}{f-\lambda_r g},\ -\frac{c}{f-\lambda_r g}\right),$$

and that the tangents at these points are

$$x+\lambda_r y=0,$$

provided that r runs through the values 1, 2, 3 in succession, and that $\lambda_1, \lambda_2, \lambda_3$ are the three roots of the cubic† in λ, viz.,

$$c\lambda^3+B\lambda^2+2H\lambda+A=0 \ldots \quad \ldots \quad \ldots \quad \ldots \qquad \text{(V)}$$

Case ii. The system (2) includes *four* parabolas, whose Cartesian equations are of the form:

$$(a+3k_r)x^2+2(h+\tfrac{3}{2}k_r^2)xy+(b+k_r^3)y^2+2gx+2fy+c=0, \qquad \text{(VI)}$$

provided that r runs through the values 1, 2, 3, 4, and that k_1, k_2, k_3, k_4 are the four roots of the biquadratic in k viz.,

$$(a+3k)\,(b+k^3)=(h+\tfrac{3}{2}k^2)^2. \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad \text{(VII)}$$

---

* The three sextactic conics will be hereafter referred to as a triad of "*cognate*" sextactic conics, and their related sextactic points will be termed "*cognate*". That is to say, two sextactic points are *cognate* or *non-cognate* according as they are or are not *co-tangential*. So the adjunct "cognate", when applied to sextactic points is synonymous with *co-tangential*, the common tangential being of course a point of inflexion of the cubic. Thus a bicursal cubic Γ must be said to possess nine triads of '*cognate*' sextactic conics and nine associated triads of "*cognate*" sextactic points.

†As usual, the capital letters (A, B, C, F, G, H) denote the co-factors of the corresponding small letters (a, b, c, f, g, h) in the determinant:

$$\begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix}.$$

Case iii. The system (2) includes *three* rectangular hyperbolas, whose Cartesian equations are of the type:

$$(a+3m_r)x^2+2(h+\tfrac{3}{2}m_r^2)xy+(b+m_r^3)y^2+2gx+2fy+c=0, \quad \text{(VIII)}$$

provided that r runs through the values 1, 2, 3 and that m_1, m_2, m_3, are the three roots of the cubic in m, viz.,

$$(a+3m)+(b+m^3)-2(h+\tfrac{3}{2}m^2)\cos w=0, \quad \ldots \quad \text{(IX)}$$

(w denoting the obliquity of the Cartesian axes).

Case iv. The system (2) includes *four* improper conics (i. e., conics composed of pairs of right lines), whose equations are of the form:

$$(a+3n_r)x^2+2(h+\tfrac{3}{2}n_r^2)xy+(b+n_r^3)y^2+2gx+2fy+c=0, \quad \text{(X)}$$

provided that r runs through the values 1, 2, 3, 4, and that n_1, n_2, n_3, n_4 are the roots of the biquadratic in n, viz.,

$$\begin{vmatrix} a+3n, & h+\tfrac{3}{2}n^2, & g \\ h+\tfrac{3}{2}n^2, & b+n^3, & f \\ g\ , & f\ , & c \end{vmatrix}=0. \quad \ldots \quad \text{(XI)}$$

If (ξ_r, η_r) be the two constituent lines of the *improper* conic (X) for any of the four values of n_r, satisfying the equation (XI), and if we set

$$\zeta_r = x+n_r.\,y,$$

then the equation (II) or (III) of the original cubic Γ can be alternatively put in each of the four forms, viz.,

$$\xi_r\,\eta_r\,y=\zeta_r^3, \quad (r=1,2,3,4). \quad \ldots \quad \text{(XII)}.$$

Remarking that the four lines of the type $\{\zeta_r\}$ all pass through the inflexion O, and that the related harmonic polar (say, ζ), viz.,

$$gx+fy+c=0$$

is the *common* polar line of O *w. r. t.* the different conics of the system (2),—including, as special varieties, the four line-pairs of the type $\{\xi_r, \eta_r\}$—and interpreting (XII) geometrically, we are squarely led to an *alternative* proof of the following known result:—

If O be any one of the nine points of inflexion (real or imaginary) of a bicursal cubic Γ, the remaining eight points of inflexion can be grouped into

four pairs, such that the two inflexions of each pair are collinear with O, and that their related tangents —of the type $\{\xi_r, \eta_r\}$*—intersect somewhere on the harmonic polar* ζ *of* 0.

Art 3. For the sake of brevity we shall now introduce the following notations:—

$$\left.\begin{aligned} S_\lambda &\equiv S+3\lambda x^2+3\lambda^2 xy+\lambda^3 y^2 \\ &\equiv (a+3\lambda)\,x^2+2\,(h+\tfrac{3}{2}\lambda^2)\,xy+(b+\lambda^3)\,y^2+2gx+2fy+c \end{aligned}\right\} \quad \ldots \quad \text{(I)}$$

and $T_\lambda \equiv x+\lambda y$. ... ... (II)

Accordingly, the equation of the original cubic Γ, viz.,

$$S.y - x^3 \quad \ldots \quad \ldots \quad \text{(III)}$$

can be alternatively put in the form

$$S_\lambda . y = T_\lambda^3. \quad \ldots \quad \ldots \quad \ldots \quad \text{(IV)}$$

It is hardly necessary to mention that, interpreted geometrically, the equation

$$S_\lambda = 0 \ldots \quad \ldots \quad \ldots \quad \text{(V)}$$

defines, for varying values of the parameter λ, a family of ∞^1 conics of double osculation, whilst the equation

$$T_\lambda = 0 \quad \ldots \quad \ldots \quad \text{(VI)}$$

defines the pencil of corresponding chords of (double) osculation, (passing, of course, through the point of inflexion O)

If we now select three *arbitrary* conics of the system (V) by ascribing three *arbitrary* values (say, λ_1, λ_2, λ_3) to λ, we can re-write (III) in each of the three symbolic forms:

$$S_{\lambda r}.y = (x+\lambda_r y)^3, \quad (r=1, 2, 3). \quad \ldots \quad \text{(VII)}$$

If, then, l, m, n denote the constants

$$\lambda_2-\lambda_3, \quad \lambda_3-\lambda_1, \quad \lambda_1-\lambda_2$$

respectively, the three equations of the type (VII) are easily seen to lead to the following irrational form (of Γ), viz.,

$$l\,S_{\lambda_1}^{\frac{1}{3}}+m\,.\,S_{\lambda_2}^{\frac{1}{3}}+n\,S_{\lambda_3}^{\frac{1}{3}}=0. \quad \ldots \quad \text{(VIII)}$$

The net result is that the *equation of a bicursal cubic Γ can be represented in the symbolic irrational form (VIII), provided that $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$ are an arbitrary triad of cognate conics of double osculation, (belonging to any one of the nine systems)*.

We may remark in passing that the conics $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$ of (VIII) may, as a special case, consist of

(i) the three *cognate* sextactic conics included in the system $\{S_\lambda\}$

or (ii) *any three* of the four pairs of tangents

$$(\xi_1, \eta_1), (\xi_2, \eta_2), (\xi_3, \eta_3), \text{ and } (\xi_4, \eta_4),$$

drawn respectively to Γ at the four pairs of inflexions, collinear with the (inflexion) O (Art. 2).

Finally, let us select (at random) two cognate conics of double osculation S_{λ_1}, S_{λ_2} and then describe an *arbitrary* conic U through their (four) points of intersection. So we may write

$$U \equiv S_{\lambda_1} + k.\, S_{\lambda_2},$$

where k is an arbitrary parameter.

There is no difficulty in re-writing the equation (III) of Γ in the modified form:

$$(1+k)\, x^3 + y\, [3\, (\lambda_1 + k\lambda_2)\, x^2 + 3\, (\lambda_1^2 + k\lambda_2^2)\, xy + (\lambda_1^3 + k\lambda_2^3)\, y^2 - U] = 0.$$

Interpreting this equation geometrically, we come to conclude that, *if S_{λ_1}, and S_{λ_2} be any two cognate conics of double osculation of a given bicursal cubic Γ, an arbitrary conic U, drawn through the four points of intersection (real or imaginary) of S_{λ_1}, S_{λ_2} must cut Γ at six points, collinear in pairs with the related point of inflexion.*

In the next article we shall refer to certain loci and envelopes, connected with a family of cognate conics of double osculation, viz., $\{S_\lambda\}$.

Art. 4. Scrutinising the *point-equation* of $\{S_\lambda\}$ as well as its *tangential* equation, one can easily verify that Chasles' characteristics (μ, ν) for the system are given by

$$\mu = 3 \quad \text{and} \quad \nu = 4$$

This corroborates the results, (arrived at in Art. 2) viz., that $\{S_\lambda\}$ contains, within its fold, *four* parabolas and *three* rectangular hyperbolas.

Now the centre-locus (Ω) of $\{S_\lambda\}$—which can be anticipated to be a curve of degree v (i.e., 4)—is easily obtained in the form :

$$\begin{vmatrix} 1, & \frac{3}{2}x, & 0, & hx+by+f, & 0 \\ 0, & y, & \frac{3}{2}x, & 0, & hx+by+f \\ \frac{3}{2}, & 3x, & ax+hy+g, & 0, & 0 \\ 0, & \frac{3}{2}y, & 3x, & ax+hy+g, & 0 \\ 0, & 0, & \frac{3}{2}y, & 3x, & ax+hy+g \end{vmatrix} = 0.$$

By *a' priori* reasoning one can easily substantiate the following statements concerning the quartic Ω :-

(i) that the four asymptotes of Ω are parallel respectively to the axes of the four parabolas, included in the family $\{S_\lambda\}$;

and (ii) that the four points of intersection of Ω with the harmonic polar ζ (of O), viz.,

$$\zeta \equiv gx+fy+c=0$$

are precisely the points of intersection of the four pairs of inflexional tangents, symbolised as

$$(\xi_1, \eta_1), (\xi_2, \eta_2), (\xi_3, \eta_3) \text{ and } (\xi_4, \eta_4) \qquad \text{in Art. 2.}$$

Next the envelope of the asymptotes of $\{S_\lambda\}$ can, without much difficulty, be shewn to be a curve of the 14th class, touching the eight inflexional tangents (just mentioned) and having the line at infinity for a multiple tangent.

Furthermore the locus of the foci of $\{S_\lambda\}$ can be identified as a curve of the 12th degree, *confocal with the original cubic* Γ.

Interested readers may, at their discretion, investigate other loci and envelopes, intrinsically related to a family of conics of double osculation.

SECTION II

(Invariants, covariants and contravariants of special triads of cognate conics of double osculation)

Art. 5. —Starting with a bicursal cubic Γ, let us, as before, take one of the nine points of inflexion as the origin O of Cartesian axes, and represent (after the manner of Art. 2) the associated family of conics of double osculation in the compact form:

$$\left.\begin{array}{l} S\lambda_r \equiv S+3\lambda_r x^2+3\lambda_r^2 . xy+\lambda_r^3 y^2=0, \\ \text{i.e.,}\ (a+3\lambda_r)x^2+2(h+\tfrac{3}{2}\lambda_r^2)xy+(b+\lambda_r^3)y^2+2gx+2fy+c=0, \end{array}\right\} \quad . \quad . \quad . \quad (\mathrm{I})$$

it being postulated that λ_r is a variable parameter.

Let us now select an *arbitrary* triad of conics of the system, viz.,

$$(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}) \quad . \quad . \quad . \quad (\mathrm{II})$$

by ascribing *arbitrary* values $\lambda_1, \lambda_2, \lambda_3$ to the parameter.

In connection with (II), we shall introduce the three notations :

(a) $M\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$,

(b) $\mathcal{J}\,(S_{\lambda_1}\, S_{\lambda_2}, S_{\lambda_3})$,

and (c) $\phi\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$

to denote respectively the M-invariant[1], the Jacobian covariant[2] and the cubic contravariant[3].

---

1. The M-invariant of three ternary quadratics U, V, W is the simplest rational function of the co-efficients, which, equated to zero, determines the condition for the expression

$$p_1U+p_2V+p_3W$$

to be rendered a perfect square by an appropriate choice of the constants p_1, p_2, p_3.

2. As is well-known, the Jacobian-covariant is the locus of a point, whose polars *w. r. t.* the three conics are concurrent.

3. The cubic contravariant of three conics is the simplest function of the line-

Deferring for the present the discussion of (*b*) and (*c*) let us now concentrate our attention upon (*a*).

Employing the standard method of Higher Algebra, we can verify without much trouble that the M-invariant, attaching to (II), is identical (save as to a multiplicative constant) with the determinant

$$\begin{vmatrix} A+c\lambda_1^3, & A+c\lambda_2^3, & A+c\lambda_3^3 \\ B+3c\lambda_1, & B+3c\lambda_2, & B+3c\lambda_3 \\ H-\frac{3}{2}c\lambda_1^2, & H-\frac{3}{2}c\lambda_2^2, & H-\frac{3}{2}c\lambda_3^2 \end{vmatrix}$$

provided, of course, that the redundant factor

$$(\lambda_2-\lambda_3)(\lambda_3-\lambda_1)(\lambda_1-\lambda_2)$$

is omitted.

Accordingly we may in all fairness set

$$M(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}) = \begin{vmatrix} A+c\lambda_1^3, & A+c\lambda_2^3, & A+c\lambda_3^3 - \frac{3}{2}c \\ B+3c\lambda_1, & B+3c\lambda_2, & B+3c\lambda_3 \\ H-\frac{3}{2}c\lambda_1^2, & H-\frac{3}{2}c\lambda_2^2, & H-\frac{3}{2}c\lambda_3^2 \end{vmatrix} \begin{vmatrix} \lambda_1^2, \lambda_2^2, \lambda_3^2 \\ \lambda_1, \lambda_2, \lambda_3 \\ 1, 1, 1 \end{vmatrix} \quad ..(III)$$

$$= 3A + 2H(\lambda_1+\lambda_2+\lambda_3) + B(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2) + 3c\lambda_1\lambda_2\lambda_3$$

Our next objective is to characterise geometrically the triad of conics (II), qualified by the condition.

$$\left.\begin{aligned} &M(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}) = 0, \\ \text{i.e.,}\ &3A+2H(\lambda_1+\lambda_2+\lambda_3)+B(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)+3c\lambda_1\lambda_2\lambda_3 = 0 \end{aligned}\right\} \quad (IV)$$

To that end it is necessary to attend to the following obvious facts:—

(i) that the harmonic polar (ζ) of the inflexion O, viz.,

$$\zeta \equiv gx+fy+c = 0$$

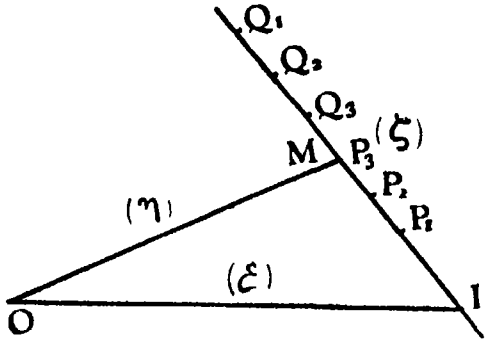
represents the *common* polar line of O *w.r.t.* all conics of the system $\{S_{\lambda_r}\}$—not excepting S_{λ_1}, S_{λ_2}, S_{λ_3};

and (ii) that the equation of the pair of tangents, drawn from O to S_{λ_r} is

$$(B+3c\lambda_r)x^2-2(H-\tfrac{3}{2}c\lambda_r^2)xy+(A+c\lambda_r^3)y^2=0. \quad \ldots \quad (V)$$

coordinates (l, m, n), which must vanish in order that the line may cut the conics in pairs of points in involution.. (Cf. Salmon's *Conic Sections* (1911), Arts. 388 (b) and 389 (a).

Suppose now (as shewn in the annexed figure) that the harmonic polar (ζ) intersects the three conics $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$ respectively at the three point-pairs: $(P_1, Q_1), (P_2, Q_2), (P_3, Q_3)$. ... . (VI)



Then, because of (i), the three line-pairs viz ,

$$(OP_1, OQ_1),\ (OP_2, OQ_2) \text{ and } (OP_3, OQ_3) \quad \ldots \quad \ldots \quad \ldots \quad \text{(VII)}$$

are respectively the three pairs of tangents, drawn from 0 to $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$. Hence by (ii), the three line-pairs are represented by the Cartesian equation (V), viz.,

$$(B+3c\lambda_r)x^2-2(H-\tfrac{3}{2}c\lambda_r^2)xy+(A+c\lambda_r^3)y^2=0, \quad \ldots \quad \ldots \quad \text{(VIII)}$$

provided that r is allowed to run through the values 1, 2, 3.

It is now a pleasant job to verify that the assumed relation (IV)—which is the same as

$$\begin{vmatrix} A+c\lambda_1^3\ , & A+c\lambda_2^3\ , & A+c\lambda_3^3 \\ B+3c\lambda_1\ , & B+3c\lambda_2\ , & B+3c\lambda_3 \\ H-\tfrac{3}{2}c\lambda_1^2, & H-\tfrac{3}{2}c\lambda_2^2, & H-\tfrac{3}{2}c\lambda_3^2 \end{vmatrix}=0 \quad \ldots \quad \ldots \quad \text{(IX)}$$

signifies geometrically that the three line-pairs (VII), defined analytically by (VIII), belong to the *same* involution,—or, what is the same thing—that the three point-pairs (VI) make up an involution. If, then, (L, M) be the two *focal points* of the point-involution (VI), the lines (OL, OM) must be the two *focal lines* of the line-involution (VII).

Furthermore the three point-pairs (P_1, Q_1), (P_2, Q_2) and (P_3, Q_3) being each harmonically conjugate with the two foci (L, M), it follows that the polars of the three points:

$$P_1, P_2, P_3,$$

with respect to *any one* of the three conics $S_{\lambda 1}$, $S_{\lambda 2}$, $S_{\lambda 3}$ pass respectively through the three points:

$$Q_1, Q_2, Q_3,$$

and *vice versa*. If we now pay heed to (i), we are led to infer that the triangle OLM is *self-conjugate* with respect to each of the three conics $S_{\lambda 1}$, $S_{\lambda 2}$, $S_{\lambda 3}$. Thus the relation (IV) or (IX) affirms the existence of a triangle, self-conjugate to all the three conics.

Further reference to Analytical Projective Geometry makes it clear that, subject to any of the equivalent relations (IV), (IX), the two focal lines (ξ, η)—i e., (OL, OM)—of the line-involution formed by (VII) are representable in the Cartesian form:

$$3\xi\eta \equiv 3x^2+2(\lambda_1+\lambda_2+\lambda_3)xy+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)y^2 \quad 0. \quad \ldots \quad \ldots \quad \ldots (X)$$

A more *direct* method of confirming this result is to verify (by Elementary Analytical Geometry) that the *expanded* form of the relation

$$M(S_{\lambda 1}, S_{\lambda 2}, S_{\lambda 3}) = 0,$$

viz, $3A+2H(\lambda_1+\lambda_2+\lambda_3)+B(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)+3C\lambda_1\lambda_2\lambda_3=0$ is interpretable as the necessary and sufficient condition that each of the three line-pairs (VII) represented by (VIII) may be harmonically conjugate with the line-pair (X).

The geometrical interpretation of (IV) being thus almost complete, we may summarise our conclusions as under :—

The invariant relation :

$$M(S_{\lambda 1}, S_{\lambda 2}, S_{\lambda 3}) = 0$$

represents the necessary and sufficient condition for the three conics of double osculation viz.,* $S_{\lambda 1}$, $S_{\lambda 2}$, $S_{\lambda 3}$ *to possess a common self-conjugate triangle* Δ.

* We may remark incidentally that the possession of a *common* self-conjugate triangle by three conics implies, in general, *three* distinct conditions, whereas the vanishing of their M-invariant amounts to a *single* condition. So it stands to reason

Further the aforesaid condition being fulfilled, the sides (ξ, η, ζ) *of the triangle* Δ *are given by the Cartesian equations:*

$$\zeta \equiv gx+fy+c=0$$

and $$3\,\xi\eta \equiv 3x^2+2\,(\lambda_1+\lambda_2+\lambda_3)\,xy+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)\,y^2=0.$$

Before we finish this article we shall utilise a familiar lemma of Analytical Geometry that the Jacobian of three conics, possessing a common self-conjugate triangle Δ, is a *degenerate* cubic, composed of three right lines, which are none other than the sides of Δ Applying this lemma in the above context we are at once driven to the conclusion that, when the M-invariant of S_{λ_1}, S_{λ_2}, S_{λ_3} vanishes, the three conics must have a common self-conjugate triangle, whose sides (ξ, η, ζ), taken together, constitute the degenerate Jacobian curve J $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$

A *direct* proof of this result will be one among many items of business to be disposed of in the next article.

Art. 6.—We shall now deal with the Jacobian curve $J(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$, mentioned in (*b*) of Art. 5. By the traditional method of Differential Calculus, the Jacobian of three *arbitrary* conics (of double osculation)

---

that the M-invariant vanishes for a triad of conics endowed with a *common* self-conjugate triangle, but that the converse is *not* true under *normal* circumstances, in other words, three conics, having a *zero* M-invariant, may or may not have a common self-conjugate triangle In fact, the possession of a common self-conjugate triangle by a triad of conics, qualified by a *zero* M-invariant, must be regarded as *accidental* rather than *natural*.

It is hardly necessary to point out that the triad of conics, considered as above, belongs to a *special* category. As a matter of fact *two* out of the three conditions—ordinarily needed to ensure the existence of a self-polar triangle- have been automatically fulfilled by S_{λ_1}, S_{λ_2}, S_{λ_3}, because of their being *cognate* conics of double osculation of a cubic. The *third* condition, which has yet to be fulfilled and which is practically the only condition that counts, is

$$M\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0$$

This explains why and how this single condition is not only necessary but also sufficient for the three conics to have a common self-conjugate triangle.

viz., S_{λ_1}, S_{λ_2}, S_{λ_3} is readily obtained in the form :

$$\begin{vmatrix} (a+3\lambda_1)x+(h+\tfrac{3}{2}\lambda_1^2)y+g, & (h+\tfrac{3}{2}\lambda_1^2)x+(b+\lambda_1^3)y+f, & gx+fy+c \\ (a+3\lambda_2)x+(h+\tfrac{3}{2}\lambda_2^2)y+g, & (h+\tfrac{3}{2}\lambda_2^2)x+(b+\lambda_2^3)y+f, & gx+fy+c \\ (a+3\lambda_3)x+(h+\tfrac{3}{2}\lambda_3^2)y+g, & (h+\tfrac{3}{2}\lambda_3^2)x+(b+\lambda_3^3)y+f, & gx+fy+c \end{vmatrix} = 0,$$

which can be put in the form :

$$(gx+fy+c)\times\left\{3x^2.\begin{vmatrix} 1 & \lambda_1 & \lambda_1^2 \\ 1 & \lambda_2 & \lambda_2^2 \\ 1 & \lambda_3 & \lambda_3^2 \end{vmatrix}+2xy\begin{vmatrix} 1 & \lambda_1 & \lambda_1^2 \\ 1 & \lambda_2 & \lambda_2^3 \\ 1 & \lambda_3 & \lambda_3^3 \end{vmatrix}+y^2\begin{vmatrix} 1 & \lambda_1^2 & \lambda_1^3 \\ 1 & \lambda_2^2 & \lambda_2^3 \\ 1 & \lambda_3^2 & \lambda_3^3 \end{vmatrix}\right\}=0,$$

i. e., $$(gx+fy+c)\left\{3x^2+2(\lambda_1+\lambda_2+\lambda_3)xy+(\lambda_2\lambda_3+\lambda_3\lambda+\lambda_1\lambda_2)y^2\right\}=0,$$

i.e., $$\zeta\xi\eta=0,$$

where the three lines ξ, η, ζ have the same significance as in Art. 5. That the harmonic polar ζ should form part of the Jacobian cubic is a foregone conclusion, considering that the line ζ is the common polar of a certain point (viz , O) *w. r. t.* the three conics S_{λ_1}, S_{λ_2}, S_{λ_3} and that reciprocally the polars of any point on ζ w.r.t S_{λ_1}, S_{λ_2}, S_{λ_3} are concurrent, (the point of concurrence being O).

Thus the verification of the result, promised in the concluding portion of the previous article, is now complete ; nay, we have proved something more. For, the above result has nothing to do with the evanescence or non-evanescence of the M-invariant; in other words S_{λ_1}, S_{λ_2}, S_{λ_3} may be three *perfectly* arbitrary conics selected out of the system (S_{λ_r}). For the sake of clarity, we may finalise our result in the following manner :

No matter the M-invariant viz.,

$$M\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$$

is or is not zero, the order-cubic viz.,

$$\mathcal{J}\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0,$$

associated with any three cognate conics of double osculation viz.,

S_{λ_1}, S_{λ_2} S_{λ_3}, *is permanently an improper cubic curve, composed of the three right lines* ζ, ξ, η *defined by*

$$\zeta \equiv gx+fy+c=0$$

and $3\xi\eta \equiv 3x^2+2(\lambda_1+\lambda_2+\lambda_3)\,xy+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)y^2=0.$

The special feature, attaching to the triad of conics $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$, *restricted by the condition*

$$M\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0$$

is that the three constituent lines (ξ, η, ζ) *of the Jacobian make up a triangle, self-conjugate with respect to the three conics.*

As an illustration of the afore-mentioned proposition let us consider the triad of six-pointic conics, included in the system $\{S_\lambda\}$.

Referring to (V) of case i (Art. 2), we note that, if $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$ denote the three sextactic conics of the family $\{S_\lambda\}$, $\lambda_1, \lambda_2, \lambda_3$ must be the three roots of the cubic:

$$c\lambda^3+B\lambda^2+2H\lambda+A=0,$$

so that

$$\lambda_1+\lambda_2+\lambda_3=-\frac{B}{c}, \qquad \lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2=\frac{2H}{c} \qquad \text{and} \qquad \lambda_1\lambda_2\lambda_3=-\frac{A}{c}.$$

Hence, by (III) of Art. 5,

$$M\,(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=3A+2H\times\left(-\frac{B}{c}\right)+B\times\frac{2H}{c}+3c\left(-\frac{A}{c}\right)=0.$$

Also the joint equation of (ξ, η), –viz., (X) of Art. 5—simplifies to

$$3x^2+2\left(-\frac{B}{c}\right)xy+\frac{2H}{c}y^2=0,$$

i. e.,

$$3cx^2-2\,Bxy+2Hy^2=0.$$

Joining this special result to the other more general results proved heretofore, we can formulate our final conclusions in the following garb:—

The necessary and sufficient condition for three cognate conics of double osculation viz., $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$ *to claim a common self-conjugate triangle is*

that their M-invariant should vanish, i. e., that the parametres λ_1, λ_2, λ_3, *should conform to the relation:*

$$3A+2H(\lambda_1+\lambda_2+\lambda_3)+B(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)+3c\lambda_1\lambda_2\lambda_3=0.$$

Subject to this condition, the sides of the common self-conjugate triangle are simply the three right lines (ξ, η, ζ) *which constitute the degenerate Jacobian curve*

$$\mathcal{J}(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0,$$

so that the equations of the three lines are

$$\zeta\equiv gx+fy+c=0$$

and $$3\xi\eta\equiv 3x^2+2(\lambda_1+\lambda_2+\lambda_3)xy+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)y^2=0.$$

A remarkably special triad of conics of the above description is that composed of the three sextactic conics, which belong to the system and whose parameters λ_1, λ_2, λ_3 *are the three roots of the cubic in* λ, *viz.,*

$$c\lambda^3+B\lambda^2+2H\lambda+A=0.$$

Furthermore the common self-conjugate triangle of these three (sextactic) conics is formed by the harmonic polar:

$$\zeta\equiv gx+fy+c=0,$$

and the line-pair (ξ, η) *given by*

$$3c\xi\eta\equiv 3cx^2-2Bxy+2Hy$$

Art. 7.—We shall now offer general criticism on an *arbitrary* triad of conics of double osculation.

General reasoning shews that *four* conditions have to be satisfied in order that a conic may have *double osculation* with a cubic. So in order that three *given* conics U, V, W may each have double osculation with an *undefined* cubic (say, Σ), 3×4 or 12 conditions—involving the *known* constants of U, V, W and the nine *unknown or disposable* constants occurring in the analytic structure of Σ—must be fulfilled. So one can readily surmise that, *in order that three given conics U. V. W may be cognate conics of double osculation of a certain cubic* (12 —9, *i e*, 3) *three conditions must be satisfied by the conics.* This is quite in consonance with the result of the previous article, considering that the reduction of the (cubic) Jacobian to a triad of right lines is tantamount to *three* condi-

tions, and that a necessary condition for U, V W to be cognate conics of double osculation is that their Jacobian should break up into three right lines But in as much as counting of constants or of conditions is not always a safe process, we have no reason to affirm anything positively regarding the *converse* case which accordingly calls for a special scrutiny Inquisitive students may propose to examine how far (if at all) the converse propos tion is valid

Art 8 —We shall now conclude this section with a brief ref erence to the cubic contravariant

$$\phi(S_{\lambda_1}\ S_{\lambda_2}\ S_{\lambda_3})$$

— mentioned at the b ginning of Art 5 —whose vanishing expresses the criterion t at the right line given by the *line coordinates* $(l\ m\ n)$ —and therefore by the Cartesian equation

$$lx+my+n=0$$

—may intersect the three conics of double osculation viz, S_{λ_1} S_{λ_2}, S_{λ_3} in pairs of points in involution

By the prescribed method of Analytical Geometry the condition in question is easily obtained in the form

$$\begin{vmatrix} P+3\lambda_1 n^2 & Q+\lambda_1^3 n^2 & R+\frac{3}{2}\lambda_1^2 n^2 \\ P+3\lambda_2 n^2 & Q+\lambda_2^3 n^2 & R+\frac{3}{2}\lambda_2^2 n^2 \\ P+3\lambda_3 n^2 & Q+\lambda_3^3 n^2 & R+\frac{3}{2}\lambda_3^2 n^2 \end{vmatrix} = 0 \qquad \text{(I)}$$

where

$$\left.\begin{aligned} P &\equiv cl^2-2\,gln+an^2 \\ Q &\equiv cm^2-2fmn+bn^2, \\ \text{and}\quad R &\equiv clm-n(fl+gm)+hn^2 \end{aligned}\right\} \qquad \text{(II)}$$

By easy manipulations and reductions, (I) can be developed into the form

$$\left[8Q-2R(\lambda_1+\lambda_2+\lambda_3)+P(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)+3n^2\lambda_1\lambda_2\lambda_3\right]=0$$

The immediate inference is that the class cubic, which normally envelops the set of ∞^1 right lines, cutting an arbitrarily assigned triad of conics in pairs of points in involution, has, in the case of the special triad $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$, broken up into a curve of class *zero* viz, the pri-

gin ($n=0$), and a class-conic Σ, determined by the tangential equation:

$$3\lambda_1\lambda_2\lambda_3 . n^2+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2) . (cl^2-2gln+an^2)$$
$$-2(\lambda_1+\lambda_2+\lambda_3)(clm-fnl-gmn+hn^2)+3(cm^2-2fmn+bn^2)=0. \quad \text{(III)}$$

An important corollary is that *every* right line, drawn through the curve of class zero (viz., the inflexion O) cuts the series of conics $\{S_{\lambda_r}\}$ in pairs of points in involution,—a result, admitting of independent verification.

For the triad of conics $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$, qualified by the condition:

$$M(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(IV)}$$

the class-conic Σ can be easily shewn to reduce to a pair of points, so that the class-cubic, defined by the cubic contravariant, is compounded of three *points* (i.e., three curves of class zero). A moment's reflection leads to the conclusion that the triangle, formed by these points, is none other than the common self-conjugate triangle, proved to exist for the triad of conics under the condition (IV) (See Art. 5).

Section III

(Canonical forms of triads of conics S_{λ_1}, S_{λ_2}, S_{λ_3}, having a zero M-invariant)

Art. 9.—Suppose as before that S_{λ_1}, S_{λ_2}, and S_{λ_3}, are three cognate conics of double osculation, having a zero M-invariant and therefore conforming to the relations:

$$M(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}) \equiv 3A+2H(\lambda_1+\lambda+\lambda_3)+B(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)+3c\,\lambda_1\lambda_2\lambda_3$$
$$=0. \quad \ldots \quad \ldots \quad (1)$$

Then, as shewn in Art. 6, the three conics must have a common self-conjugate triangle, whose sides ζ, η, ξ are given by

$$\zeta \equiv gx+fy+c=0 \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

and $3\xi\eta \equiv 3x^2+2(\lambda_1+\lambda_2+\lambda_3)\,xy+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)\,y^2=0 \quad \ldots \quad \ldots \quad (2)$

Manifestly, then, if the individual equations of the lines ξ, η (passing through O) be written as

$$\xi \equiv x-\mu y=0 \quad \text{and} \quad \eta \equiv x-\nu y=0, \quad \ldots \quad \ldots \quad (3)$$

then μ, ν must be the two roots of the quadratic in t, viz.

$$3t^2+2(\lambda_1+\lambda_2+\lambda_3)\,t+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)=0, \quad \ldots \quad \ldots \quad (4)$$

so that

$$\left.\begin{aligned} \mu+\nu &= -\tfrac{2}{3}(\lambda_1+\lambda_2+\lambda_3), \\ \text{and}\quad \mu\nu &= \tfrac{1}{3}(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2). \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

Recollecting the familiar proposition on a triad of conics, endowed with a common self-conjugate triangle, we infer at once that there must exist nine numerical constants viz.,

$$l_1,\ m_1,\ n_1,\ l_2,\ m_2,\ n_2,\ l_3,\ m_3,\ n_3,$$

compatible with the three *identities* (in x, y), viz.

$$S_{\lambda_1} \equiv l_1\xi^2+m_1\eta^2+n_1\zeta^2, \quad \ldots \quad \ldots \quad (6)$$

$$S_{\lambda_2} \equiv l_2\xi^2+m_2\eta^2+n_2\zeta^2, \quad \ldots \quad \ldots \quad (7)$$

$$S_{\lambda_3} \equiv l_3\xi^2+m_3\eta^2+n_3\zeta^2. \quad \ldots \quad \ldots \quad (8)$$

Replacing S_{λ_1}, S_{λ_2}, S_{λ_3} by their equivalent values (in terms of x, y), viz., three expressions of the type

$$S_{\lambda_r} \equiv (a+3\lambda_r)x^2+2(h+\tfrac{3}{2}\lambda_r^2)xy+(b+\lambda_r^3)y^2+2gx+2fy+c, (r=1,2,3), \quad (9)$$

and substituting for ξ, η, ζ the functional values (in terms of x, y) as provided for by (1) and (3), we can readily convert (6), (7), (8) respectively into three identities of the type:

$$(a+3\lambda_r)x^2+2(h+\tfrac{3}{2}\lambda_r^2)xy+(b+\lambda_r^3)y^2+2gx+2fy+c$$
$$\equiv l_r(x-\mu y)^2+m_r(x-\nu y)^2+n_r(gx+fy+c)^2, \quad (r=1,2,3). \quad \ldots \quad (10)$$

Equating co-efficients of like terms in x, y, we derive relations of the type:

$$n_r = \frac{1}{c}, \quad \ldots \quad \ldots \quad \ldots \quad \text{(i)}$$

$$l_r+m_r-3\lambda_r+\frac{B}{c}, \quad \ldots \quad \ldots \quad \ldots \quad \text{(ii)}$$

$$l_r\mu+m_r\nu-\frac{H}{c}-\frac{3}{2}\lambda_r^2, \quad \ldots \quad \ldots \quad \ldots \quad \text{(iii)}$$

and

$$l_r\mu^2+m_r\nu^2-\frac{A}{c}+\lambda_r^3, \quad \ldots \quad \ldots \quad \ldots \quad \text{(iv)}$$

(r being as usual allowed to run through the values 1, 2, 3). Obviously, the equation (i) gives n_r directly, and *any* two of the other three equations viz., (ii), (iii), (iv) can be solved linearly for l_r, m_r

Needless to say, the mutual consistency of (ii), (iii), (iv) follows from the fact that the determinant:

$$\begin{vmatrix} 1, & \mu, & \mu^2 \\ 1, & \nu, & \nu^2 \\ 3\lambda_r+\frac{B}{c}, & \frac{H}{c}-\frac{3}{2}\lambda_r^2, & \frac{A}{c}+\lambda_r^3 \end{vmatrix}$$

vanishes by virtue of (I) and (5). This is as it should be, for the coexistence of the canonical forms (6), (7), (8) for $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$ is a direct consequence of their having a common self-conjugate triangle (viz., ξ, η, ζ).

Now reverting to our former topic, and solving (ii), (iii) for l_r, m_r we derive

$$\left.\begin{aligned} l_r &= \frac{\frac{H}{c}-\frac{3}{2}\lambda_r^2-(3\lambda_r+\frac{B}{c})\nu}{\mu-\nu}, \\ \text{and} \quad m_r &= \frac{(3\lambda_r+\frac{B}{c})\mu-(\frac{H}{c}-\frac{3}{2}\lambda_r^2)}{\mu-\nu}. \end{aligned}\right| (r=1, 2, 3). \qquad \ldots \quad \ldots \quad \text{(V)}$$

Joining the main results of this article to the proved results of the previous articles, we can summarise our conclusions in the undermentioned form:

The invariant relation

$$M(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})=0 \qquad \ldots \quad \ldots . \quad \text{(I)}$$

represents the necessary and sufficient condition that the three cognate conics of double osculation S_{λ_1}, S_{λ_2}, S_{λ_3} may admit of the simultaneous canonical forms :

$$\left.\begin{aligned} S_{\lambda_1} &= l_1\,\xi^2+m_1\,\eta^2+n_1\,\zeta^2, \\ S_{\lambda_2} &= l_2\,\xi^2+m_2\,\eta^2+n_2\,\zeta^2, \\ S_{\lambda_3} &= l_3\,\xi^2+m_3\,\eta^2+n_3\,\zeta^2, \end{aligned}\right\}$$

where (ξ, η, ζ) are three determinate right lines and $\{l_r\}$, $\{m_r\}$ and $\{n_r\}$ are determinate constants. Looked at from a geometrical standpoint, the three lines

ξ, η, ζ form the common self-conjugate triangle that the three conics must possess under the condition (I), *whereas the improper cubic curve made up of the three lines is none other than their Jacobian. The actual Cartesian equations to the three lines are*

$$\xi \equiv x-\mu y=0, \qquad \eta \equiv x-\nu y=0 \qquad \zeta \equiv gx+fy+c=0$$

where μ, ν are the two roots of the quadratic in t, viz.

$$3t^2+2(\lambda_1+\lambda_2+\lambda_3)t+(\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2)=0.$$

Furthermore the coefficients

$$\{l_r\}, \quad \{m_r\} \quad \text{and} \quad \{n_r\}$$

are given by

$$l_r \quad \frac{\frac{H}{c}-\frac{3}{2}\lambda_r^2-\left(3\lambda_r+\frac{B}{c}\right)\nu}{\mu-\nu},$$

$$m_r \quad \frac{\left(3\lambda_r+\frac{B}{c}\right)\mu-\left(\frac{H}{c}-\frac{3}{2}\lambda_r^2\right)}{\mu-\nu},$$

and

$$n_r=\frac{1}{c}.$$

N B.—It is hardly necessary to add that the third coefficient of the type $\{n_r\}$ is independent of r, being, as it is, equal to $\frac{1}{c}$ So $n_1=n_2=n_3=\frac{1}{c}$; still for the sake of symmetry the notations n_1, n_2, n_3 have been retained

Art. 10.—As an illustration of the general proposition of the preceding article, let us consider the triad of cognate *sextactic* conics S_{λ_1}, S_{λ_2}, S_{λ_3}, whose parameters are known to conform to the relations:

$$\lambda_1+\lambda_2+\lambda_3=-\frac{B}{c},$$

$$\lambda_2\lambda_3+\lambda_3\lambda_1+\lambda_1\lambda_2=\frac{2H}{c}$$

and

$$\lambda_1\lambda_2\lambda_3=-\frac{A}{c}.$$

Now by (4) and (5) of Art. 9 we see that μ, ν are the roots of the

quadratic in t, viz.

$$3ct^2-2Bt+2H=0, \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

so that

$$\mu+\nu=\frac{2B}{3c} \quad \text{and} \quad \mu\nu=\frac{2H}{3c}. \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Hence (V) of Art. 9 gives

$$l_r=\frac{3}{2(\nu-\mu)}\left(\lambda_r^2+2\lambda_r\nu+\frac{2B}{3c}\nu-\frac{2H}{3c}\right)$$

$$=\frac{3}{2(\nu-\mu)}\cdot\left\{(\lambda_r+\nu)^2-\left(\nu^2-\frac{2B}{3c}\cdot\nu+\frac{2H}{3c}\right)\right\} \qquad \ldots \quad \ldots \quad (3)$$

and

$$m_r=\frac{3}{2(\mu-\nu)}\cdot\left(\lambda_r^2+2\lambda_r\mu+\frac{2B}{3c}\cdot\mu-\frac{2H}{3c}\right)$$

$$=\frac{3}{2(\mu-\nu)}\cdot\left\{(\lambda_r+\mu)^2-\left(\mu^2-\frac{2B}{3c}\cdot\mu+\frac{2H}{3c}\right)\right\}. \qquad \ldots \quad (4)$$

Now by (2)

$$\nu^2-\frac{2B}{3c}\cdot\nu+\frac{2H}{3c}=\nu^2-\nu(\mu+\nu)+\mu\nu=0,$$

and

$$\mu^2-\frac{2B}{3c}\cdot\mu+\frac{2H}{3c}\quad\mu^2-\mu(\mu+\nu)+\mu\nu=0.$$

These relations follow also from the consideration that μ, ν are the roots of (1).

Hence (3) and (4) simplify to

$$l_r=\frac{3(\lambda_r+\nu)^2}{2(\nu-\mu)},$$

and

$$m_r=\frac{3(\lambda_r+\mu)^2}{2(\mu-\nu)}.$$

We may then sum up our results as under :—

The three cognate sextactic conics S_{λ_1}, S_{λ_2}, S_{λ_3} belonging to the system $\{S_{\lambda_r}\}$ can be simultaneously represented in the three canonical forms:

$$S_{\lambda_r} \equiv l_r \xi^2 + m_r \eta^2 + n_r \zeta^2, \qquad (r=1, 2, 3)$$

where the constants

$$\{l_r\}, \{m_r\}, \{n_r\}$$

are determined by

$$l_r = \frac{3(\lambda_r + \nu)^2}{2(\nu - \mu)},$$

$$m_r = \frac{3(\lambda_r + \mu)^2}{2(\mu - \nu)} \qquad (r=1, 2, 3)$$

and

$$n_r = \frac{1}{c},$$

and the three right lines ξ, η, ζ *are defined by*

$$\xi \equiv x - \mu y = 0, \quad \eta \equiv x - \nu y = 0 \quad \text{and} \quad \zeta \equiv gx + y + c = 0,$$

it being understood that μ, ν *are the two roots of the quadratic in* t, *viz.*

$$3ct^2 - 2Bt + 2H = 0.$$

SECTION IV

1. *Digression on a triad of conics with a common self-conjugate triangle*
2. *Application to a triad of cognate conics* S_{λ_1}, S_{λ_2}, S_{λ_3}, *of zero M-invariant*

Art. 11 —We know from the Theory of Higher Plane Curves that, *in general*, a uniquely determinate cubic can be found so as to have three arbitrarily assigned conics U, V, W for polar conics. Let us now proceed to examine how far this theorem is valid when the three conics happen to possess a common self-conjugate triangle (say, Δ). Then on taking Δ as the fundamental triangle of reference, we may express the *homogeneous* equations of the three conics in the respective forms:

$$U \equiv a_1\xi^2 + b_1\eta^2 + c_1\zeta^2 = 0, \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$V \equiv a_2\xi^2 + b_2\eta^2 + c_2\zeta^2 = 0, \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

and

$$W \equiv a_3\xi^2 + b_3\eta^2 + c_3\zeta^2 = 0. \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Let Σ represent the cubic, having for its homogeneous equation:

$$l\xi^3 + m\eta^3 + n\zeta^3 = 0, \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

where the parametric constants $l:m:n$ may be arbitrarily chosen.

There is no difficulty in shewing that, for any particular set of values for $l:m:n$, the Hessian of Σ is a *degenerate* cubic curve composed of three right lines (viz., the three sides ξ, η, ζ of Δ), and that the pencil of (four) tangents, drawn to Σ from an *arbitrary* point on its periphery, is *equi-anharmonic*. In point of fact, Σ belongs to a wider class of cubic curves called '*equi-anharmonic*' by Hilton.*

If now P, Q, R denote respectively the three points, whose homogeneous (i.e., projective) coordinates are

$$\left(\frac{a_1}{l}, \frac{b_1}{m}, \frac{c_1}{n}\right), \quad \left(\frac{a_2}{l}, \frac{b_2}{m}, \frac{c_2}{n}\right) \text{ and } \left(\frac{a_3}{l}, \frac{b_3}{m}, \frac{c_3}{n}\right),$$

it is easy to see that the polar conics of P, Q, R w. r. t. the cubic Σ are respectively identical with the three original conics U, V, W defined by (1), (2), (3).

If, for a *given* triad of conics U, V, W, we go on varying the ratios $l:m:n$, the cubic Σ and the triad of points P, Q, R will also vary, but, then, the geometrical property, established as above, will continue to hold good.

Thus, whereas three assigned conics U, V, W are, *in general*, polar conics of three *determinate* points P, Q, R w. r. t. a *determinate* cubic curve Σ, the numbers of such cubics and also of the correlated triad of points (P, Q, R) will become *two-fold infinity* in the particular case, when U, V, W have a common self-conjugate triangle. †To be precise, *three conics having a common self-conjugate triangle ABC can be designated as polar conics, belonging to any one of a family of* ∞^2 *equi-anharmonic cubics, which have, for their common Hessian, the degenerate cubic made up of the three lines* (BC, CA, AB).

---

*See Hilton's "*Plane Algebraic Curves*" (1920), P 238, Ex. 6.

†Regard being had to the fact that the M-invariant vanishes for the triad of conics (U, V, W), possessing a common self-conjugate triangle, it is crystal-clear that Dr. Salmon's remark ["Conic Sections" (1911), Art. 389 (c)] viz., "*If the invariant M vanishes, an exception occurs and the conics cannot all be derived from the same cubic,*" does not seem to fit in with established facts.

Art. 12.—We can now readily apply the results of the foregoing article to a triad of conics of double osculation $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$, belonging to a given cubic and possessing a zero M-invariant.

As shewn in Sec. III, the triad of conics will then have a common self-conjugate triangle (say, Δ) and their *homogeneous* equations, referred to Δ, will assume the respective forms:

$$S_{\lambda_1} \equiv l_1\xi^2 + m_1\eta^2 + n_1\zeta^2 = 0,$$
$$S_{\lambda_2} \equiv l_2\xi^2 + m_2\eta^2 + n_2\zeta^2 = 0, \qquad \ldots \quad \ldots \qquad \text{(I)}$$
and
$$S_{\lambda_3} \equiv l_3\xi^2 + m_3\eta^2 + n_3\zeta^2 = 0,$$
the coefficients

$$(l_1, m_1, n_1, \quad l_2, m_2, n_2, \quad l_3, m_3, n_3)$$
being defined by (V) of Art. 9.

Let Σ denote the cubic

$$p\xi^3 + q\eta^3 + r\zeta^3 = 0. \qquad \ldots \quad \ldots \qquad \text{(II)}$$
where the coefficients $p:q:r$ are arbitrary.

It is a tane affair to verify that the three conics $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$ given by (I), are respectively the polar conics of the three points, whose homogeneous or projective coordinates are

$$\left(\frac{l_1}{p}, \frac{m_1}{q}, \frac{n_1}{r}\right), \quad \left(\frac{l_2}{p}, \frac{m_2}{q}, \frac{n_2}{r}\right) \quad \text{and} \quad \left(\frac{l_3}{p}, \frac{m_3}{q}, \frac{n_3}{r}\right).$$
with respect to the cubic Σ.

It is needless to point out that, when the parameters p, q, r, are allowed to vary, the equation (II) will define a family of ∞^2 equianharmonic cubics, any one of which will have the given conics $(S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3})$ for a triad of polar conics.

Of course the above result holds good even when $S_{\lambda_1}, S_{\lambda_2}, S_{\lambda_3}$, are a triad of cognate sextactic conics.

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1948

PARTS V & VI] SECTION A [VOL. 17

ON THE BENDING OF AN ELLIPTIC PLATE UNDER CERTAIN DISTRIBUTIONS OF LOAD. (II)*

H. M. SENGUPTA

(Communicated by Prof. N. M. Basu, D.Sc.)

(Received Feb 28, 1948)

In the present paper the author proposes to determine the deflexion of the central plane of a thin elliptic plate made of isotropic elastic material, clamped at the edge under the action of a load of weight W distributed uniformly over a half of the plate bounded by either of the principal axes

Let the bounding ellipse of the central plane of the plate be given by,

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}=1. \qquad (a>b>0)$$

If we introduce elliptic co-ordinates by the transformation

$$x+iy=c\cosh(\xi+i\eta). \qquad (c>0)$$

We have

$$x=c\cosh\xi\cos\eta$$
$$y=c\sinh\xi\sin\eta$$

Then $\xi=$ const. and $\eta=$ const. give a family of confocal ellipses and hyperbolas cutting each other at right angles. In particular $\xi=\alpha$ would represent the boundary, provided

$$a=c\cosh\alpha \text{ and } b=c\sinh\alpha.$$

*This forms a part of a thesis approved for the award of the Ph. D. degree of the University of Dacca. A few verbal and explanatory changes have been made here and there

We shall consider two cases.

CASE I.

We shall first assume that the semi-ellipse

$$0 \leqslant \xi < a$$

$$-\frac{\pi}{2} < \eta < \frac{\pi}{2}$$

is subjected uniformly to the load of weight W while the other half is free from pressure.

The pressure at any point of the semi-ellipse $0 \leqslant \xi < a$;

$-\frac{\pi}{2} < \eta < \frac{\pi}{2}$ is then given by $p = \frac{2W}{\pi ab}$.

If we take the plate to be of thickness $2h'$ the deflexion u should satisfy the differential equation

$$DV_1^4 w = p$$

in the semi-ellipse $0 \leqslant \xi < a$ and $-\frac{\pi}{2} < \eta < \frac{\pi}{2}$ (where $D = \frac{2}{3} \cdot \frac{Eh'^3}{1-\sigma^2}$, E and σ being the Young's Modulus and Poisson's ratio respectively of the isotropic elastic material of which the plate is made.)
and $V_1^4 w = 0$ in the semi-ellipse.

$$0 \leqslant \xi < a$$

$$\frac{\pi}{2} < \eta < \frac{3\pi}{2}.$$

Also it must satisfy the boundary conditions.

$$w = \frac{\partial \omega}{\partial \xi} = 0 \text{ over } \xi = a.$$

Further the stresses must be continuous throughont the plate including the boundary.

Here we take the positive direction of the z-axis in the direction towards which the weight acts.

CASE II. Next we suppose that the semi-ellipse

$$0 < \xi < a$$

$$0 < \eta < \pi$$

is subjected to the load.

If we denote the corresponding deflexion by w we must have

$$D\, V_1^4 w = p$$

in the semi-ellipse

$$0 < \xi < a$$
$$0 < \eta < \pi$$

and $$V_1^4 w = 0$$

in the semi ellipse $0 < \xi < a$, $\pi < \eta < 2\pi$

The stresses arising out of u must be continuous throughout the plate including the boundary

Also $\bar{w}$ must satisfy the conditions

$$w - \frac{\partial w}{\partial \xi} \quad 0 \quad \text{over } \xi - a$$

The problems in hand will be solved by combining the solutions of two known problems Of these one is simple and its solution is well known The other is obtained by a slight modification of the solution of the problem of the bending of a thin semi elliptic plate under uniform pressure where the elliptic boundary is clamped and the straight boundary (which may either be the minor axis or the major axis) is freely supported This latter problem was solved by Prof Galerkin*

The deflexion of the central plane of a thin elliptic plate with clamped edge under the action of a uniform pressure $\frac{1}{2}p$ at a point is given by

$$w_1 = \frac{1}{16}\frac{p}{D}\left(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}\right)^2 \Big/ \left(\frac{3}{a^4} + \frac{3}{b^4} + \frac{2}{a^2 b^2}\right)^{**} \qquad (1)$$

On the other hand Prof Galerkin shows that the deflexion of the central plane of a semi elliptic plate given by $0 \leqslant \xi \leqslant \eta$, $-\pi/2 \leqslant \eta \leqslant \pi/2$ whose elliptic boundary is clamped, and the straight boundary is freely

*Prof B G G lerkin,—Messenger of Mathematics Vol LII (1923) pp 99-109

**Elasticity by Love page 484 (Fourth edition)

The result in due of Prof G H. Bryan

supported under uniform pressure $\frac{1}{2}p$ is given by

$$w_2 = L(3+4\cosh 2\xi+\cosh 4\xi)(3+4\cos 2\eta+\cos 4\eta) + (k_1\cosh\xi + A_1\cosh 3\xi)\cos\eta$$

$$+\sum_{n=2}^{\infty}\Big\{A_{2n-3}\cosh(2n-3)\xi + k_{2n-1}\cosh(2n-1)\xi + A_{2n-1}\cosh(2\eta+1)\xi\Big\}\cos(2n-1)\eta \quad . \quad . \quad . \quad (2)\dagger$$

where $L = \dfrac{pc^4}{3072\,D}$

We can easily verify that the series for w_2 formally satisfies the differential equation

$$DV_1^4 w_2 = \tfrac{1}{2}p$$

at every point of the semi-ellipse $0 \leqslant \xi < a$, $-\frac{\pi}{2} < \eta < \frac{\pi}{2}$ excepting at the focus $\xi = 0$, $\eta = 0$.

The conditions for supported edge along the minor axis ($x=0$ or $\eta = \pm\pi/2$) are

$$w_2 = 0 \text{ and } G = 0$$

where G is the expression for flexural couple arising out of w_2.

It is easy to show that the above conditions reduce to

$$w_2 = 0 \text{ and } \frac{\partial^2 w_2}{\partial\eta^2} = 0$$

over $\eta = \pi/2$ and $\eta = -\pi/2$. And both these are formally satisfied by the series for w_2 over the minor axis.

The conditions for supported edge along the major axis may be shown to be

$$w = 0 \text{ and } \frac{\partial^2 w}{\partial\eta^2} = 0 \text{ over } \eta = 0, \text{ and } \eta = \pi$$

and

$$w = 0 \text{ and } \frac{\partial^2 w}{\partial\xi^2} = 0 \text{ over } \xi = 0 \ (0 < \eta < \pi)$$

---

†Prof. Galerkin uses a slightly different but essentially the same form for the biharmonic part of the above expression.

Vide—B. G. Galerkin—Messenger of Mathematics—Vol. 52 (1923) p. 106.

Also remembering that*

$$f(\eta) = \frac{768}{\pi} \sum_{n=1}^{\infty} \frac{(-)^{n+1} \cos(2n-1)\eta}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)}$$

where

$$f(\eta) = 3 + 4\cos 2\eta + \cos 4\eta \quad \text{for } -\pi/2 < \eta < \pi/2$$

and $$f(\eta) = -(3 + 4\cos 2\eta + \cos 4\eta) \quad \text{for } \pi/2 < \eta < 3\pi/2.$$

The conditions $w_2 - \frac{\partial w_2}{\partial \xi} = 0$ over $\xi = a$ are satisfied by the following values of k's and A's

$$k_1(\sinh 4a + 2\sinh 2a) = \frac{K(\sinh 4a - 7\sinh 2a)}{3.1.1.3.5} \tag{3}$$

$$A_1(\sinh 4a + 2\sinh 2a) = -\frac{K\sinh 2a}{1.1.3.5} \tag{4}$$

$$\begin{aligned} K_{2n-1}(\sinh 4na + 2n\sinh 2a) \\ &= -A_{2n-3}\{2\sinh(4n-2)a + (2n-1)\sinh 4a\} \\ &\quad - \frac{(-)^{n+1}K\{(2n-3)\sinh(2n+2)a + (2n+5)\sinh 2na\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)} \end{aligned} \tag{5}$$

$$\begin{aligned} A_{2n-1}(\sinh 4na + 2n\sinh 2a) \\ &= A_{2n-3}\{\sinh(4n-4)a + (2n-2)\sinh 2a\} \\ &\quad + \frac{(-)^{n+1}K\{2n-5)\sinh 2na + (2n+3)\sinh(2n-2)a\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)} \end{aligned} \tag{6}$$

where $K = \frac{3072 L\cosh^3 a}{\pi} - \frac{pc^4\cosh^3 a}{\pi D}$

Prof. Galerkin merely states that the equations obtained from the boundary conditions can be solved.

We may now assert that the function w_3 defined by

$$\begin{aligned} w_3 = L(3 + 4\cosh 2\xi + \cosh 4\xi)(3 + 4\cos 2\eta + \cos 4\eta) \\ + (k_1\cosh\xi + A_1\cosh 3\eta)\cos\eta \\ + \sum_{n=2}^{\infty}\left\{A_{2n-3}\cosh(2n-3)\xi + k_{2n-1}\cosh(2n-1)\xi + A_{2n-1}\cosh(2n+1)\xi\right\} \\ \times\cos(2n-1)\eta \end{aligned} \tag{7}$$

* Prof. B. G. Galerkin—The Messenger of Mathematics Vol LII (1923) p. 107.

in the region $0 \leqslant \xi \leqslant a, -\frac{\pi}{2} < \eta \leqslant \frac{\pi}{2}$

and
$$u_3 = -I(3+4\cosh 2\xi+\cosh 4\xi)(3+4\cos 2\eta+\cos 4\eta) + (k_1\cosh\xi + A_1\cosh 3\xi)\cos\eta$$
$$+\sum_{n=3}^{\infty}\left\{A_{2n-1}\cosh(2n-3)\xi + k_{2n-1}\cosh(2n-1)\xi + A_{2n-1}\cosh(2n+1)\xi\right\} \times\cos(2n-1)\eta \qquad (8)$$

in the region $0 < \xi < a, \frac{\pi}{2} < \eta < \frac{3\pi}{2}$

with the same values for L and k's and A's formally satisfies the equations

$$DV_1^4 u_3 = \tfrac{1}{2}p \quad \text{in } 0 < \xi < a, -\frac{\pi}{2} < \eta < \frac{\pi}{2},$$

excepting at the focus $\xi = 0, \eta = 0$

and $DV_1^4 u_3 = -\frac{1}{2}p$ in $0 < \xi < a, \frac{\pi}{2} < \eta < \frac{3\pi}{2}$,

excepting at the focus $\xi = 0, \eta = \pi$

Also the boundary conditions $u_3 = \frac{\partial u_3}{\partial \xi} = 0$

are formally satisfied over the elliptic boundary $\xi = a$

We now consider the function

$$w = u_1 + u_3 \qquad (9)$$

The function w formally satisfies the differential equation

$DV_1^4 w = p$, at every point of the region

$0 < \xi < a \quad -\pi/2 < \eta < \pi/2$

excepting at the focus $\xi = 0, \eta = 0$

It formally satisfies the equation

$V_1^4 w = 0$ at every point of the region

$0 \leqslant \xi < a, \pi/2 < \eta < 3\pi/2$

excepting at the focus $\xi = 0, \eta = \pi$

Also it formally satisfies the conditions

$$w = \frac{\partial w}{\partial_\nu} = 0 \text{ over } \xi = a$$

ν being the direction of the inward drawn normal to the edge line $\xi = a$

w is therefore expected to represent the deflexion of the central place of a thin elliptic plate clamped along the edge $\xi = a$ carrying a load of weight w spread uniformly over the semi-ellipse

$$0 \quad \xi < a; \; -\pi/2 < \eta < \pi/2.$$

We have now to consider convergence of the series giving the deflexion of the elliptic plate.

w_1 stands for

$$\frac{1}{16}\frac{p}{D}\left(1 - \frac{x^2}{b^2} - \frac{y^2}{b^2}\right)^2 \Big/ \left(\frac{3}{a^4} + \frac{3}{b^4} + \frac{2}{a^2 b^2}\right)$$

which is necessarily finite and continuous throughout the elliptic plate. It possesses finite and continuous partial derivatives of all orders with respect to x and y and also mixed derivatives. In fact derivatives of order higher than 4 are all zero and $D_1^4 \; w_1 = \frac{p}{2}$. Again

$$L(3 + 4\cosh 2\xi + \cosh 4\xi) \times (3 + 4\cos 2\eta + \cos 4\eta) = \frac{64 L x^4}{c^4} \qquad (10)$$

Denoting this part by f and the series

$$(k_1 \cosh \xi + A_1 \cosh 3\xi) \cos \eta$$

$$\sum_{n=2}^{\infty} \{A_{2n-3} \cosh (2n-3)\xi + k_{2n-1} \cosh (2n-1)\xi + A_{2n-1} \cosh (2n+1)\xi\} \cos (2n-1)\eta$$

by F.

The deflexion may be written as

$$w = w_1 + f + F \qquad (11)$$

in region I i.e., the part of the plate for which $x \geqslant 0$ and

$$w = w_1 - f + F$$

in region II in the part of the plate for which $x \leqslant 0$.

Now the function

$$\psi = f \quad \text{for } x > 0$$

and

$$\psi = -f \quad \text{for } x < 0$$

is evidently continuous at $x = 0$.

Partial derivatives of ψ with respect to y are all zero. Partial derivatives upto the third order of ψ with respect to x are continuous throughout. While the partial derivative of ψ of the fourth order with respect is x has a discontinuty at $x = 0$. In fact

$$\frac{\partial^4 \psi}{\partial x^4} = \frac{24 \times 64 L}{c^4} \quad \text{for } x > 0$$

and

$$\frac{\partial^4 \psi}{\partial x^4} = -\frac{24 \times 64 L}{c^4} \quad \text{for } x < 0$$

so

$$D V_1^4 \psi = \frac{p}{2} \quad \text{for } x > 0$$

and

$$D V_1^4 \psi = -\tfrac{1}{2} p \quad \text{for } x < 0.$$

It follows also that contributions to stress resultants and stress couples due to this part of the deflexion function are finite and cortinuous throughout the elliptic plate. Moreover they vanish over the minor axis.

Putting $f_{2n-1} = \sinh 4na + 2n \sinh 2a$ we have from the recurrence formulae obtained in the previous section

$$A_1 f_1 = -K \frac{\sinh 2a}{1.1.3.5}$$

$$A_3 f_3 = A_1 f_1 - K \left[\frac{\sinh 4a}{1.3.5.7} - \frac{\sinh 2a}{1.1.3.5} \right]$$

$$A_5 f_5 = A_3 f_3 + K \left[\frac{\sinh 6a}{3.5.7.9} + \frac{\sinh 4a}{1.3.5.7} \right]$$

$$A_7 f_7 = A_5 f_5 - K \left[\frac{\sinh 8a}{5.7.9.11} + \frac{\sinh 6a}{3.5.7.9} \right]$$

$$\cdots \qquad \cdots \qquad \cdots$$

$$A_{2n-1} f_{2n-1} = A_{2n-3} f_{2n-3} + (-)^{n+1} K \left[\frac{\sinh 2na}{(2n-3)(2n-1)(2n+1)(2n+3)} + \frac{\sinh 2(n-1)a}{(2n-5)(2n-3)(2n-1)(2n+1)} \right.$$

Adding

$$A_{2n-1}f_{2n-1}=\frac{(-)^{n+1}K\sinh 2n\alpha}{(2n-3)(2n-1)(2n+1)(2n+3)}$$

giving a neat formula for the value of A_{2n-1}.

viz, $$A_{2n-1}=\frac{(-)^{n+1}K\sinh 2n\alpha}{(2n-3)(2n-1)(2n+1)(2n+3)f_{2n-1}}. \tag{13}$$

Now, since $\alpha>0$,

$$f_{2n-1}=\sinh 4n\alpha+2n\sinh 2\alpha>\sinh 4n\alpha>0.$$

So, we can show that

$$|A_{2n-1}|<\frac{K}{(2n-3)(2n-1)(2n+1)(2n+3)\,e^{4n\alpha}} \tag{14}$$

for $n\geqslant 2$.

Also since

$$k_{2n-1}f_{2n-1}=-A_{2n-3}\{2\sinh(4n-2)\alpha+(2n-1)\sinh 4\alpha\}$$
$$\frac{K(-)^{n-1}\{(2n-3)\sinh(2n+2)\alpha+(2n+5)\sinh 2n\alpha\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)}.$$

We can without difficulty show that

$$|k_{2n-1}|\leqslant\frac{\overline{G}}{(2n-5)(2n-3)(2n-1)(2n+1)\,e^{4n\alpha}} \tag{15}$$

for sufficiently large n, where $\overline{G}$ is a positive constant independent of n.

Now, take the series

$$F_1=\sum_{n=1}^{\infty}k_{2n-1}\cosh(2n-1)\xi\cos(2n-1)\eta$$

we have

$$|\,k_{2n-1}\cosh(2n-1)\xi\cos(2n-1)\eta\,|$$
$$\leqslant|k_{2n-1}|\cosh(2n-1)|\xi|$$
$$\leqslant\frac{\overline{G}\;e^{-\alpha}}{(2n-5)(2n-3)(2n-1)(2n+1)}e^{(2n-1)(|\xi|-\alpha)}$$

for sufficiently large n.

The series therefore converges absolutely and uniformly for all η and all ξ such that $-a \leqslant \xi \leqslant a$

It therefore converges absolutely and uniformly in both the variables ξ and η, throughout the elliptic plate including the boundary $\xi = a$. F_1, the sum of the series is therefore continuous throughout the plate including the boundary. Also it is easy to see that $\frac{\partial F_1}{\partial \xi}$ is obtained by term-by-term differentiation of the series for F_1, for the differentiated series is likewise absolutely and uniformly convergent throughout the elliptic plate inlcuding the boundary. $\frac{\partial F_1}{\partial \xi}$ is moreover continuous throughout the plate including the boundary.

Take

$$F_2 = \sum_{n=2}^{\infty} A_{2n-3} \cosh (2n-3)\xi \cos (2n-1)\eta.$$

Now,

$$\begin{aligned} & | A_{2n-3} \cosh (2n-3)\xi \cos (2n-1)\eta | \\ \leqslant \quad & | A_{2n-3} | \cosh (2n-3)\xi \\ \leqslant \quad & \frac{K \cosh (2n-3)\xi}{(2n-5)(2n-3)(2n-1)(2n+1)e^{2n\alpha}} \\ \leqslant \quad & \frac{K e^{(2n-3)|\xi|}}{(2n-5)(2n-3)(2n-1)(2n+1)e^{2n\alpha}} \\ = \quad & \frac{K e^{(2n-3)(|\xi|-\alpha)}}{e^{3\alpha}(2n-5)(2n-3)(2n-1)(2n+1)} \quad \text{for sufficiently large } n. \end{aligned}$$

$\sum_{n=2}^{\infty} A_{2n-3} \cosh (2n-3)\xi \cos (2n-1)\eta$ is therefore absolutely and uniformly convergent for all η and all ξ such that $|\xi| \leqslant a$. The sum F_2 therefore is continuous throughout the plate including the boundary. Also $\frac{\partial F_2}{\partial \xi}$ is obtained by-term-by term differentiation, for the differentiated series is absolutely and uniformly convergent throughout the plate including the boundary.

The same remark applies to the series

$$F_3 = \sum_{n=1}^{\infty} A_{2n-1} \cosh (2n-1)\xi \cos (2n \quad 1)\eta$$

The value of $F = F_1 + F_2 + F_3$ and also $\frac{\partial F}{\partial \xi}$ for $\xi = \alpha$ is therefore obtained by putting $\xi = \alpha$ in the series for F and the series for $\frac{\partial F}{\partial \xi}$ respectively. This justifies the method by which the values of the constants k's and A's were obtained. It is plain that derivatives of F of all orders in ξ and η can be had by formal term-by-term differentiation of the series for F at all points in the interior of the ellipse $\xi = \alpha$ Partial derivatives with respect to ξ and η upto the second order can be had by formal term-by-term differentiation at all points of the elliptic plate including the boundary.

Following the plan adopted in a previous note, we can easily show that

$$F_1 = \sum_{n=1}^{\infty} k_{2n-1} \cosh (2n-1)\, \xi \cos (2n-1)\eta$$

is equal to the real part of the series

$$\sum_{n=1}^{\infty} k_{2n-1} P_{2n-1}(z)$$

where $P_{2n-1}(z)$ is some polynomial of degree $(2n-1)$.

The series $\sum_{n=1}^{\infty} k_{2n-1} \cosh (2n-1)\xi \cos (2n-1)\eta$ is uniformly convergent in any closed region contained within the ellipse $\xi = \alpha$, the region of uniform convergence extending upto the boundary of the ellipse.

The same is true of the series

$$\sum_{n=1}^{\infty} k_{2n-1} \sinh (2n-1)\xi \sin (2n-1)\eta.$$

So the series

$$\sum_{n=1}^{\infty} k_{2n-1} P_{2n-1}(z)$$

represents an analytic function throughout the interior of the ellipse. The derivatives of the function represented by $\sum_{n=1}^{\infty} k_{2n-1} P_{2n-1}(z)$ can be had by term-by-term differentiation throughout the interior of the ellipse. Its real part, viz., F_1 is plane harmonic throughout the interior of the ellipse, i.e., it satisfies the equation

$$V_1^2 F_1 = 0 \quad \text{throughout} \quad 0 \leqslant \xi < a.$$

All partial derivatives of F_1 with respect to x and y and also mixed derivatives exist and are continuous throughout the interior of the plate, thus giving continuous contribution to stress resultants and couples in that region.

The series

$$F_2 + F_3 = \sum_{n=2}^{\infty} A_{2n-3} \cosh(2n-3)\xi \cos(2n-1)\eta$$

$$+ \sum_{n=1}^{\infty} A_{2n-1} \cosh(2n+1)\xi \cos(2n-1)\eta$$

which may be written as

$$\sum_{n=1}^{\infty} A_{2n-1} \{ \cosh(2n+1)\xi \cos(2n-1)\eta$$

$$+ \cosh(2n-1)\xi \cos(2n+1)\eta \}$$

throughout the elliptic plate including the boundary, is the real part of the function defined by the series,

$$(x - iy) \sum_{n=1}^{\infty} A_{2n-1} P_{2n}(z)$$

where $P_{2n}(z)$ is some polynomial of degree $2n$ in z.

We easily prove that the series $\sum_{n=1}^{\infty} A_{2n-1} P_{2n}(z)$ defines an analytic

function throughout the interior of the elliptic plate. Partial Derivatives of the function defined by the series are continuous throughout the interior of the plate and in this region F_2+F_3 satisfies the equation

$$V_1^4(F_2+F_3)=0.$$

Contribution to stress resultants and stress couples arising out of the part (F_2+F_3) are therefore finite and continuous throughout the interior of the plate. We have now only to check if these are finite and continuous upto the boundary of the plate

Now we proved elsewhere that for sufficiently large n

$$|k_{2n-1}| \leqslant \frac{\bar{G}}{(2n-5)(2n-3)(2n-1)(2n+1)e^{2n\alpha}}$$

and $$|A_{2n-1}| \leqslant \frac{K}{(2n-3)(2n-1)(2n+1)(2n+3)e^{2n\alpha}}$$

where K, $\bar{G}$ are positive constants independent of n.
Consider the series

$$\sum_{n=1}^{\infty} k_{2n-1}(2n-1)^2\cosh(2n-1)\xi\cos(2n-1)\eta$$

i.e., the series that is obtained by differentiating the series for

$$F_1=\Sigma\, k_{2n-1}\cosh(2n-1)\xi\cos(2n-1)\eta$$

term by term twice with respect to ξ.

The general term of the derived series is

$$(2n-1)^2 k_{2n-1}\cosh(2n-1)\xi\cos(2n-1)\eta$$

on the other hand

$$\begin{aligned}(2n-1)^2 &|k_{2n-1}\cosh(2n-1)\xi\cos(2n-1)\eta| \\ &\leqslant (2n-1)^2|k_{2n-1}|\cosh(2n-1)\xi \\ &\leqslant \frac{(2n-1)^2\bar{G}\cosh(2n-1)\xi}{(2n-5)(2n-3)(2n-1)(2n+1)e^{2n\alpha}} \\ &\leqslant \frac{\bar{G}e^{(2n-1)|\xi|}}{(2n-5)(2n-3)e^{2n\alpha}} \\ &= \frac{\bar{G}e^{-\alpha}}{(2n-5)(2n-3)}e^{(2n-1)(|\xi|-\alpha)}\end{aligned}$$

The range of uniform convergence of the series therefore extends upto the boundary $\xi=\alpha$ So the term-by-term differentiation of the series is possible for all ξ which lie in the range $0<\xi<\alpha$ and also the left hand differentiation with respect to ξ is possible for $\xi=\alpha$ Further the sum of the derived series represents the corresponding differential co-efficient of the sum of the original series and is a function that is continuous upto the boundary $\xi=\alpha$. The same statement is true for all partial derivatives upto the second order with respect to ξ and η.

Thus stress resultants and couples depending on derivatives upto the second order are finite and continuous throughout the plate including the boundary.

Now the normal shearing stress across an arc s, is defined by

$$N=-D\frac{\partial}{\partial\nu}V_1^2 w$$

where ν is the direction of the normal to the curve.

The contribution to N by F_1 is zero.

On the other hand

$$\begin{aligned}V_1^2(F_2+F_3)=32/c^2[&A_1\cosh\xi\cos\eta+2A_3(\cosh\xi\cos\eta+\cosh 3\xi\cos 3\eta)\\&+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\&+nA_{2n-1}\{\cosh\xi\cos\eta+\cosh 3\xi\cos 3\eta+\ldots\\&\qquad+\cosh(2n-1)\xi\cos(2n-1)\eta\}\\&+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots]\end{aligned}$$

The above result is valid throughout the plate including the boundary excepting the foci.

Now across any curve

$$\xi=\alpha',\quad\text{where}\quad 0<\alpha'<\alpha$$

$$\partial/\partial\nu\, V_1^2\,(F_2+F_3)$$

$$=h\frac{\partial}{\partial\xi}V_1^2\,(F_2+F_3).$$

By formal term by term differention we have

$$\partial/\partial\xi\ V_1^2\,(F_2+F_3)$$
$$=32/c^2\,[A_1\sinh\xi\cos\eta+2A_3\,(\sinh\xi\cos\eta+3\sinh 3\xi\cos 3\eta]$$
$$+3A_5\,(\sinh\xi\cos\eta+3\sinh 3\xi\cos 3\eta+5\sinh 5\xi\cos 5\eta)$$
$$+\ \ldots\ldots\ldots\ \ldots\ldots\ldots\ldots$$
$$+nA_{2n-1}\,\{\sinh\xi\cos\eta+3\sinh 3\xi\cos 3\eta$$
$$+\ldots+(2n-1)\sinh(2n-1)\xi\cos(2n-1)\eta\}$$
$$+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots].$$

In what follows we restrict our attention to values of $\xi\geqslant 0$.

For throughout the plate ξ can never assume negative values

$$n\,|A_{2n-1}\,\{\sinh\xi\cos\eta+3\sinh 3\xi\cos 3\eta+\ldots$$
$$+(2n-1)\sinh(2n-1)\,\xi\cos(2n-1)\,\eta\}|$$
$$\leqslant n|A_{2n-1}|\{\sinh\xi+3\sinh 3\xi+5\sinh 5\xi$$
$$+\ldots+(2n-1)\sinh(2n-1)\xi\}$$
$$\leqslant\tfrac{1}{2}\,n|\,A_{2n-1}\,|\,(e^{\xi}+3e^{3\xi}+5e^{5\xi}+\ldots+(2n-1)\,e^{(2n-1)\,\xi}).$$

On the other hand we can show that in the range $0<\beta\leqslant\xi\leqslant\alpha$

$$0<e^{\xi}+3e^{3\xi}+5e^{5\xi}+\ldots+(2n-1)\,e^{(2n-1\xi)}$$
$$<\frac{4\,(2n+1)\,e^{(2n+3)\alpha}}{\Delta^4}\quad\text{where}$$
$$\nabla=(e^{2\alpha}-1).$$

In the above ring-shaped region, we have therefore

$$n|A_{2n-1}\,\{\sinh\xi\cos\eta+3\sinh 3\xi\cos 3\eta+\ldots$$
$$+\ldots+(2n-1)\sinh(2n-1)\xi\cos(2n-1)\eta|$$
$$\leqslant\frac{4n(2n+1)\,|\,A_{2n-1}\,|\,e^{(2n+3)\,\alpha}}{(e^{2\alpha}-1)^2}$$
$$\leqslant\frac{2K\,e^{3\alpha}}{(e^{2\alpha}-1)^2}\cdot\frac{1}{(2n-3)(2n-1)}.$$

So the series for $\frac{\partial}{\partial\xi}\ V_1^2(F_2+F_3)$ converges absolutely and uniformly in the closed ring-shaped region $0<\beta\leqslant\xi\leqslant\alpha$ including the boundaries.

The sum of the series therefore is the correct value for $\frac{\partial}{\partial \xi} V_1^2 (F_2+F_3)$ throughout the ring-shaped region in which the function is finite and continuous. Thus the normal shearing stress N across an arc $\xi=$ const. is certainly continuous in the ring-shaped region including the boundaries.* It was previously proved that N is continuous in the open domain $0 \leqslant \xi < a$. We have therefore proved that N is finite and continuous throughout the plate including the boundary.

We have thus proved that

$$w = w_1 + f + F \text{ in } 0 \leqslant \xi \leqslant a; -\pi/2 \leqslant \eta \leqslant \pi/2$$

and

$$\bar{w} = w_1 - f + F \text{ in } 0 \leqslant \xi \leqslant a; \quad \pi/2 \leqslant \eta \leqslant 3\pi/2$$

represent a function continuous throughout the plate including the boundary. It satisfies the differential equations

$$D \nabla^4 w = p \text{ in } 0 \leqslant \xi \leqslant a; -\pi/2 < \eta < \pi/2$$

and

$$D \nabla w = 0 \text{ in } 0 \leqslant \xi < a; \quad \pi/2 < \eta < 3\pi/2.$$

Further the stress-resultant N and the stress couples G and H as derived from w are finite and continuous throughout the plate including the boundary $\xi = a$.

Further $$w = \frac{\partial w}{\partial \nu} = 0 \quad \text{on } \xi = a.$$

It is only at the points that lie on the minor axis that the differential equation of equilibrium has not been shown to hold. It was so, because the function defining the deflexion is such that the partial derivative of the fourth order with respect to x has a discontinuity across that line.

We therefore take a rectangle bounded by the straight lines.

$$x = -l, \qquad x = l$$

$$y = y_2, \qquad y = y_1$$

where $$-b < y_2 < y_1 < b$$

and $l(>0)$ is small enough to ensure that the above rectangle lies

*Likewise, we can prove that the normal shearing stress N' across an arc $\eta=$ const, is continuous in the same ring-shaped region including the boundaries.

completely within the ellipse. The value of the integral $\int N ds$ taken along the edges of the above rectangle can easily be shown to equal $-\frac{2Wl(y_1-y_2)}{\pi ab}$ which is just the weight of that part of the proposed load which happens to be contained within the rectangle. It follows that there is no concentrated point load or line load anywhere on the minor axis.

w as defined above, therefore, represents the deflexion of the central plane of a thin elliptic plate clamped along the edge ($\xi=a$) carrying a load of weight W spread uniformly over the semi-ellipse

$$0<\xi<a\ ;-\frac{\pi}{2}<\eta<\frac{\pi}{2}.$$

CASE II

The deflexion of the central plane of a thin elastic plate of the shape of a semi-ellipse bounded by the major axis (say the semi-ellipse $0\leqslant\xi\leqslant a$; $0\leqslant\eta\leqslant\pi$) under the action of a uniform pressure $\frac{1}{2}p$ where the elliptic boundary is clamped and the straight boundary is merely supported has also been given by Prof. Galerkin. He takes

$$w_4=L(3-4\cosh 2\xi+\cosh 4\xi)(3-4\cos 2\eta+\cos 4\eta)$$
$$+(l_1\sinh\xi+B_1\sinh 3\xi)\sin\eta$$
$$\sum_{2n=1}^{\infty}\left\{B_{2n-3}\sinh(2n-3)\xi+l_{2n-1}\sinh(2n-1)\xi+B_{2n-1}\sinh(2n-1)\xi\right\}$$
$$\times\sin(2n-1)\eta^{*} \qquad (16)$$

where $L=\frac{pc^4}{3072D}$ and the constants l's and B's are to be determined.

---

* The expression

$$E=B_1\sinh 3\xi\sin\eta+\sum_{n=1}^{\infty}\left\{B_{2n-3}\sinh(2n-3)\xi+B_{2n-1}\sinh(2n+1)\xi\right\}$$
$$\sin(2n-1)\eta$$

is a formal solution of the differentiation in equation $\nabla_1^4 E=0$, in elliptic coordinates. It was given in a slightly different but essentially the same form by Prof. Galerkin. (Vide—B. Galerkin—Messenger of Mathematics Vol 52 (1923) pp 108-9.) See also Timpe—Mathematische Zeitscrift Vol. 17 (1923) P. (92.)

The function w_4 formally satisfies the differential equation

$$D\nabla_1^4 w_4 = \tfrac{1}{2}p$$

at every point of the semi-ellipse

$$0 < \xi < a$$
$$0 < \eta < \pi$$

It also satisfies $w_4 = \dfrac{\partial^2 w_4}{\partial \eta^2} = 0$ over $\eta = 0$ and $\eta = \pi$ and also the conditions

$$w_4 = \frac{\partial^2 w_4}{\partial \xi^2} = 0 \text{ over } \xi = 0.$$

The condition of being freely supported along the major axis is thus formally satisfied.

On the other hand remembering that *

$$f(\eta) = \frac{768}{\pi} \sum_{n=1}^{\infty} \frac{\sin(2n-1)\eta}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)}$$

where

$$f(\eta) = 3 - 4\cos 2\eta + \cos 4\eta \quad \text{for } 0 \leqslant \eta \leqslant \pi$$

and

$$f(\eta) = -(3 - 4\cos 2\eta + \cos 4\eta) \text{ for } \pi \leqslant \eta \leqslant 2\pi.$$

The conditions $w_4 = \dfrac{\partial w_4}{\partial \xi} = 0$ over $\xi = a$ are satisfied by the following sets of values for the constants L's and B's.

$$L_1(\sinh 4a - 2\sinh 2a) = \frac{K'(\sinh 4a + 7\sinh 2a)}{3.1.1.3.5} \tag{17}$$

$$B_1(\sinh 4a - 2\sinh 2a) = -\frac{K'\sinh 2a}{1.1.3.5} \tag{18}$$

$$\begin{aligned} l_{2n-1}(\sinh 4na - 2n\sinh 2a) = {} & -B_{2n-3}\{2\sinh(4n-2)a - (2n-1)\sinh 4a\} \\ & -\frac{K'\{(2n-3)\sinh(2n+2)a - (2n+5)\sinh 2na\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)} \end{aligned} \tag{19}$$

$$\begin{aligned} B_{2n-1}(\sinh 4na - 2n\sinh 2a) = {} & B_{2n-3}\{\sinh(4n-4)a - (2n-2)\sinh 2a\} \\ & + \frac{K'\{(2n-5)\sinh 2na - (2n+3)\sinh(2n-2)a\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)} \end{aligned} \tag{20}$$

*Prof. B. G. Galerkin—Messenger of Mathematics. Vol. 52 (1923) p. 109.

where $$K' = \frac{3072 L \sinh^3 \alpha}{\pi} = \frac{pc^4 \sinh^3 \alpha}{\pi D}.$$

We now define the functions $w_5(\xi, \eta)$ as

$$w_5(\xi, \eta) - L(3-4\cosh 2\xi + \cosh 4\xi)(3-4\cos 2\eta + \cos 4\eta) + (l_1 \sinh \xi + B_1 \sinh 3\xi)\sin \eta$$

$$+ \sum_{n=2}^{\infty} \left\{ B_{2n-3} \sinh(2n-3)\xi + l_{2n-1} \sinh(2n-1)\xi + B_{2n-1} \sinh(2n+1)\xi \right\} \times \sin(2n-1)\eta \qquad (21)$$

in the region $0 \leqslant \xi \leqslant \alpha$; $0 \leqslant \eta \leqslant \pi$

and

$$w_5(\xi, \eta) \quad -L(3-4\cosh 2\xi + \cosh 4\xi)(3-4\cos 2\eta + \cos 4\eta) + (l_1 \sinh \xi + B_1 \sinh 3\xi)\sin \eta$$

$$+ \sum_{n=2}^{\infty} \{ B_{2n-3} \sinh(2n-3)\xi \pm l_{2n-1} \sinh(2n-1)\xi + B_{2n-1} \sinh(2n+1)\xi \} \sin(2n-1)\eta \qquad (22)$$

in the region $0 \leqslant \xi \leqslant \alpha$; $\pi \leqslant \eta \leqslant 2\pi$
with the same values for L, l's and B's.
The function w_5 formally satisfies the equation

$$DV_1^4 w_5 = \tfrac{1}{2}p \text{ in } 0 < \xi < \alpha;\ 0 < \eta < \pi$$

and $$DV_1^4 w_5 = -\tfrac{1}{2}p \text{ in } 0 < \xi < \alpha;\ \pi < \eta < 2\pi.$$

Also from the manner in which the constants l's and B's have been determined, we find that

$w_5 = \dfrac{\partial w_5}{\partial \xi} = 0$ are formally satisfied over $\xi = \alpha$

we now define the function $\bar{w}$ as

$$\bar{w} = w_1 + w_5. \qquad (23)$$

Thus the function $\bar{w}$ formally satisfies the equation

$$D V_1^4 \bar{w} = p \quad \text{over} \quad 0 < \xi < \alpha;\ 0 < \eta < \pi$$

and $$V_1^4 w = 0 \quad \text{over} \quad 0 < \xi < \alpha;\ \pi < \eta < 2\pi$$

also the conditions $w = \dfrac{\partial \bar{w}}{\partial \xi} = 0$ over $\xi = \alpha$.

So $\bar{w}$ is expected to represent the deflexion of the central plane of an elliptic plate clamped at the edge supporting a load of weight W spread uniformly over the semi-ellipse

$$0<\xi<\alpha\ ;\ 0<\eta<\pi.$$

It is now necessary to examine the expression w which formally satisfies the requirements of the problem.

It is easy to show that

$$L\,(3-4\cosh 2\xi+\cosh 4\xi)\,(3-4\cos 2\eta+\cos 4\eta) = \frac{64\,Ly^4}{C^4}\,. \quad (24)$$

Denoting the above by f' and the series

$$(l_1 \sinh \xi + B_1 \sinh 3\xi)\sin\eta$$

$$+\sum_{n=2}^{\infty}\Big\{B_{2n-3}\sinh(2n-3)\xi + l_{2n-1}\sinh(2n-1)\xi$$

$$B_{2n-1}\sinh(2n+1)\xi\Big\}\sin(2n-1)\eta$$

by F' we may write the expression for deflexion as

$$\bar{u} = w_1 + f' + F' \text{ in } 0 \leqslant \xi \leqslant \alpha\ ;\ 0 \leqslant \eta \leqslant \pi \quad (25)$$

(*i.e.*, for $y \geqslant 0$)

$$\bar{w} = w_1 - f' + F' \text{ in } 0 \leqslant \xi \leqslant \alpha ; \pi \leqslant \eta \leqslant 2\pi \quad (26)$$

(*i.e.*, for $y \leqslant 0$).

Now, the function

$$\psi' = f' \quad \text{for} \quad y \geqslant 0$$

and

$$\psi' = -f' \quad \text{for} \quad y \leqslant 0$$

is evidently continuous at $y=0$.

Partial derivatives of ψ' with respect to x are all zero. Again partial derivatives upto the third order of ψ' with respect to y are continuous throughout the plate while the partial derivatives of the fourth order with respect to y has a finite discontinuity at $y=0$

It is not even defined for $y=0$. In fact

$$\frac{\partial^4\psi'}{\partial y^4} = \frac{1536\,L}{c^4} \text{ for } y>0$$

and $$\frac{\partial^4\psi'}{\partial y^4} = -\frac{1536L}{C^4} \text{ for } y<0.$$

So $$DV_1^4\psi' = \tfrac{1}{2}p \text{ for } y>0 \textit{ i.e. } \text{in } 0<\xi<a;\ 0<\eta<\pi$$

and $$DV^4_1\psi' = -\tfrac{1}{2}p \text{ for } y<0 \textit{ i.e. } \text{in } 0<\xi<a; \pi<\eta<2\pi.$$

It is plain that contributions to stress resultants and stress couples due to ψ' are finite and continuous throughout the plate including the boundary.

We next break up the series F' as before, into three parts

$$F' = F_1' + F_2' + F_3'$$

where $$F_1' = \sum_{n=1}^{\infty} l_{2n-1} \sinh(2n-1)\xi \sin(2n-1)\eta$$

$$F_2' = \sum_{n=2}^{\infty} B_{2n-3} \sinh(2n-3)\xi \sin(2n-1)\eta$$

$$F_3' = \sum_{n=1}^{\infty} B_{2n-1} \sinh(2n+1)\xi \sin(2n-1)\eta$$

we write

$$f'_{n-1} = \sinh 4na - 2n \sinh 2a.$$

Then

$$B_1 f_1' = -\frac{K' \sinh 2a}{1 \cdot 1 \cdot 3 \cdot 5}$$

$$B_3 f_3' = B_1 f_1' + \frac{K' \{\sinh 4a + 7 \sinh 2a\}}{1 \cdot 1 \cdot 3 \cdot 5 \cdot 7}$$

$$B_5 f_5' = B_3 f_3' + \frac{K' \{\sinh 6a - 9 \sinh 4a\}}{1 \cdot 3 \cdot 5 \cdot 7 \cdot 9}$$

$$B_7 f_7' = B_5 f_5' + \frac{K' \{3 \sinh 8a - 11 \sinh 6a\}}{3 \cdot 5 \cdot 7 \cdot 9 \cdot 11}$$

... ...

$$B_{2n-1} f'_{2n-1} = B_{2n-3} f'_{2n-3} + \frac{K'\{(2n-5)\sinh 2na - (2n+3)\sinh(2n-2)a}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)}.$$

Adding we have

$$B_{2n-1} f_2'{}_{n-1} = \frac{K' \sinh 2na}{(2n-3)(2n-1)(2n+1)(2n+3)}$$

So

$$B_{2n-1}=\frac{K'\sinh 2na}{(2n-3)(2n-1)(2n+1)(2n+3)f'_{2n-1}}.$$

We can now prove that for sufficiently large n

$$|B_{2n-1}|\leqslant\frac{2K'}{(2n-3)(2n-1)(2n+1)(2n+3)e^{4na}} \tag{27}$$

Also since

$$l_{2n-1}\,f'_{2n-1}=-B_{2n-3}\{2\sinh(4n-2)a-(2n-1)\sinh 4a\}$$
$$-\frac{K'\{(2n-3)\sinh(2n+2)a-(2n+5)\sinh(2n-2)a\}}{(2n-5)(2n-3)(2n-1)(2n+1)(2n+3)}.$$

We can now show that, for sufficiently large n

$$|l_{2n-1}|\leqslant\frac{G'}{(2n-5)(2n-3)(2n-1)(2n+1)\,e^{4na}} \tag{28}$$

where G' is a positive constant independent of n.

We can easily prove that the series

$$F_1'=\sum_{n=1}^{\infty} l_{2n-1}\sinh(2n-1)\,\xi\,\sin(2n-1)\eta$$

$$F_2'=\sum_{n=1}^{\infty} B_{2n-3}\sinh(2n-3)\,\xi\,\sin(2n-1)\eta$$

$$F_3'=\sum_{n=1}^{\infty} B_{2n-1}\sinh(2n+1)\,\xi\,\sin(2n-1)\eta$$

each converges absolutely and uniformly throughout the elliptic plate including the boundary $\xi=a$. Each series therefore represents a continuous function throughout the plate including the boundary. The sum of the three series, i.e., the series for F', thus, converges absolutely and uniformly throughout the plate including the boundary. It may, therefore, be re-arranged in any way we like and the sum which remains unaltered for any re-arrangement of terms represents a function which is continuous throughout the plate including the boundary.

It is quite easy to show that $\frac{\partial F'}{\partial \xi}$ can be obtained by term-by-term differentiation of the series for F' with respect to ξ for all points

of the plate including the boundary. This justifies the process which was employed to determine the values of the constants. Further the partial derivatives of all orders of F' with respect to ξ and η and also mixed derivatives of all orders may be obtained by term-by-term differentation of the series for F' at all points within the interior of the ellipse and in that open domain they represent continuous functions. Derivatives upto the second order are however continuous upto the boundary.

We can easily show that the complex series

$$\sum_{n=1}^{\infty} l_{2n-1} (\cosh \overline{2n-1}\, \xi \cos \overline{2n-1}\, \eta + i \sinh \overline{2n-1}\, \xi \sin \overline{2n-1})\, \eta$$

transforms itself into the following series

$$\sum_{n=1}^{\infty} l_{2n-1} P_{2n-1}(z)$$

where $P_{2n-1}(z)$ is some polynomial of degree $(2n-1)$ in z.

The latter series being uniformly convergent in the interior as well as the boundary of the ellipse $\xi = a$ represents an analytic function in the interior of the elliptic plate.

The series $F_1' = \sum_{n=1}^{\infty} l_{2n-1} \sinh (2n-1)\, \xi \sin(2n-1)\eta$

being the imaginary part of a function analytic in the interior of the plate, possesses continuous partial derivatives of all orders with respect to x and y and also continuous mixed derivatives in the same domain. So the contributions to the stress-resultant N and stress couples G and H arising out of F_1' are continuous throughout the interior of the plate.

The function F_1' is harmonic throughout the interior of the elliptic plate, i.e.

$$V_1^2 F_1' = 0$$

and so $$V_1^4 F_1' = 0 \quad \text{throughout } 0 \leqslant \xi < a$$

The series

$$F_2'+F_3'=\sum_{n=1}^{\infty} B_{2n-1}\Big\{\sinh(2n+1)\xi\sin(2n-1)\eta$$

$$+\sinh(2n-1)\xi\sin(2n+1)\eta\Big\}$$

is the imaginary part of the function

$$(x-iy)\sum_{n=1}^{\infty} B_{2n-1}P_{2n}(z)$$

where $\sum_{n=1}^{\infty} B_{2n-1}P_{2n}(z)$ is a function analytic in the interior of the elliptic plate. Writing

$$\sum_{n=1}^{\infty} B_{2n-1}P_{2n}(z)=v+iv'$$

we have

$$F_2'+F_3'=xv'-yv.$$

It follows that

$$V_1^4\,(F_2'+F_3')=0 \qquad \text{throughout the interior of the elliptic plate } \xi=\alpha.$$

The contributions to the stress-resultant N and stress couples G and H arising out of $F_2'+F_3'$ are also continuous throughout the interior of the plate. Having proved that G, H and N are continuous throughout the interior of the plate we have only to consider their behaviour on the boundary.

We can easily show that the series obtained by differentiating the series for F_1', F_2' and F_3' twice with respect to ξ and η are uniformly convergent throughout the plate including the boundary $\xi=\alpha$. This shows that the stress couples G and H, depending as they do on derivatives upto the second order are continuous upto the boundary. The region of continuity of the stress-resultant N may as in the previous section be also shown to extend upto the boundary of the plate $\xi=\alpha$.

It therefore follows that the series for $\bar{w}$ defines a function that is continuous throughout the elliptic plate including the boundary. The stresses as derived from $\bar{w}$ are continuous throughout the plate including the boundary. Further $\bar{w}$ satisfies the differential equation

$$D V_1^4 = w\frac{2W}{\pi ab} \text{ in } 0 < \xi < a \; ; 0 < \eta < \pi$$

and the differential equation

$$V_1^4 \bar{w} = 0 \quad \text{in } 0 < \xi < a; \; \pi < \eta < 2\pi.$$

Further let us take the rectangle

$$x = x_2; \; x = x_1$$
$$y = -l; \; y = l$$

where $-a < x_2 < x_1 < a$; and where l (>0) is small enough to ensure that the rectangle lies completely within the ellipse $\xi = a$. The rectangle evidently contains the length $(x_1 - x_2)$ of the major axis. Now, the value of the integral $\int N\, ds$ taken along the edges of the rectangle may very easily be proved to be equal to $-\frac{2\, Wl\,(x_1 - x_2)}{\pi ab}$. This shows that there is no concentrated point load or a line load anywhere on the major axis.

Finally $w = \frac{\partial \bar{w}}{\partial \nu} = 0$ are satisfied over the boundary $\xi = a$.

Thus $\bar{w}$ represents the deflexion of the mid plane of a thin elliptic plate clamped along the edge $\xi = a$, carrying a load of weight W spread uniformly over the semi-ellipse $0 < \xi < a$, $0 < \eta < \pi$.

I am indebted to Prof. N. M. Basu for the kind interest he has taken in the preparation of the paper.

NOTE ON CIRCULAR CUBICS AND BICIRCULAR QUARTICS

By

HARIDAS BAGCHI, M. A., PH. D.,

Lecturer in Pure Mathematics and Officiating Head of the Department of Pure Mathematics, Calcutta University, Calcutta.

Communicated by Dr. K. M. Basu, D.Sc., F. N. A. Sc., Lecturer in Applied Mathematics, University College of Science, 92, Upper Circular Road, Calcutta—9

Received on September 3, 1948.

INTRODUCTION

The object of the present paper is to investigate, among other things, certain novel properties of a circular cubic and also of a bicircular quartic, with special reference to the normals, that can be drawn from the centres of inversion to the associated focal conics. Notice has also been taken of the rectangular hyperbola, that has been shown to pass through the feet of the afore-said normals.

The whole paper has been divided into three Sections, of which the first two deal respectively with a circular cubic and a bicircular quartic. Section III finally disposes of certain digressional matter on the construction of differential equations of the first order, whose singular solutions shall be *assigned* (plane) curves, e.g., a parabola or an ellipse or a hyperbola or a circular cubic or a bicircular quartic.

It has been tacitly assumed throughout the paper that the circular cubic or the bicircular quartic under discussion is of the *unrestricted* type, so that it is bicursal, i.e., has *unit* deficiency or *genus*. The *unicursal* type of circular cubic or bicircular quartic, being of a comparatively simple type, has been practically ignored in this paper.

Although the subject under discussion is classical in origin, the paper is believed to embody a considerable amount of original matter.

Other papers, bearing on this subject, are in course of preparation and are expected to be published in the near future

SECTION I

(*Circular Cubics*)

Art. 1. As was pointed out by Dr Casey, a bicursal circular cubic Γ possesses, in general, four circles of inversion $(\pi, \pi_1, \pi_2, \pi_3)$ and four focal parabolas $(\Sigma, \Sigma_1, \Sigma_2, \Sigma_3)$, so correlated that the cubic Γ is describable as the envelope of the set of circles, having their centres on any one of the focal conics (say Σ_r) and cutting the corresponding circle of inversion (say, π_r) at right angles As a matter of fact, if any of the circles (say, π) and the associated parabola (Σ) be represented in the respective Cartesian forms

$$(x-\alpha)^2+(y-\beta)^2=k^2 \quad \text{and} \quad y^2=4a(x+a) \quad . \quad . \quad . \quad (1)$$

the equation of the bicursal circular cubic can be thrown into the form:

$$x(x^2+y^2)+(2a-\alpha)(x^2+y^2)+(c^2-4a\alpha)x-4a\beta y$$
$$+\{2a(\alpha^2+\beta^2)-c^2\alpha\}=0, \qquad (I)$$

where $$c^2\equiv k^2-\alpha^2-\beta^2. \quad . \quad . \quad . \quad (2)$$

By algebraic manipulations, (I) can be turned successively into each of the three equivalent forms, viz

$$x(x^2+y^2)+(2a_r-\alpha_r)(x^2+y^2)+(c_r^2-4a_r\alpha_r)x-4a_r\beta_r y$$
$$+\{2a_r(\alpha_r^2+\beta_r^2)-c_r^2\alpha_r\}=0, \ (r=1, 2, 3), \quad . \quad (II)$$

provided that the constants $\{a_r\}$, $\{c_r\}$, $\{\alpha_r\}$, $\{\beta_r\}$ and $\{\lambda_r\}$ are determined by the relations:

$$\left.\begin{aligned} a_r=a+\lambda_r, \quad \alpha_r=\alpha+2\lambda_r, \quad \beta_r=\frac{a\beta}{a+\lambda_r} \\ \text{and} \qquad c_r^2=c^2+4\lambda_r(2a+\alpha)+8\lambda_r^2, \end{aligned}\right\} \quad . \quad . \quad . \quad (III)$$

and λ_1, λ_2, λ_3 are the three *non-zero* roots of the biquadratic in λ, viz :

$$\frac{a^2\beta^2}{a+\lambda}+(a-\lambda)(\alpha+2\lambda)^2-4a\lambda(\alpha+2\lambda)-c^2\lambda-a(\alpha^2+\beta^2)=0. \qquad (IV)$$

In view of (2) and (III), the equation for k_r is evidently

$$k_r^2=k^2-\alpha^2-\beta^2+(\alpha+2\lambda_r)^2+\frac{a^2\beta^2}{(a+\lambda_r)^2}$$
$$+4\lambda_r(2a+\alpha)+8\lambda_r^2, \ldots\ldots (r=1, 2, 3).$$

Comparison of the Cartesian equations (I) and (II) at once leads to the conclusion that the other three circles of inversion (π_1, π_2, π_3) and the corresponding focal parabolas $(\Sigma_1, \Sigma_2, \Sigma_3)$ are given by

$$(x-\alpha_r)^2+(y-\beta_r)^2=k_r^2 \quad \text{and} \quad y^2=4a_r(x+a_r), \ (r=1,2,3).$$

The very *forms* of the four focal parabolas $(\Sigma, \Sigma_1, \Sigma_2, \Sigma_3)$ at once proclaim their *confocal* character, the common focus, viz. O, being, of course, the double focus of the cubic Γ. The four centres of inversion, viz.

$$(\alpha_1, \beta_1), (\alpha_2, \beta_2), (\alpha_3, \beta_3) \quad \text{and} \quad (\alpha, \beta)$$

will be henceforth denoted by the letters A B, C, D (taken in order). The subsidiary relations, viz.

$$\left.\begin{array}{ll} 2a_r-\alpha_r=2a-\alpha, & a_r\beta_r=a\beta, \quad c_r^2-4a_r\alpha_r=c^2-4a\alpha \\ \text{and} \quad 2a_r(\alpha_r^2+\beta_r^2)-c_r^2\alpha_r=2a(\alpha^2+\beta^2)-c^2\alpha, & \ldots \end{array}\right\} \begin{array}{l}(r=1,2,3)\\ \ldots \quad \text{(V)}\end{array}$$

which follow automatically from (III), or as a consequence of (I) and (II) being *identical*, will be made use of in the succeeding articles.

Art. 2. Selecting indifferently one of the focal parabolas (say, Σ), viz.,

$$y^2=4a(x+a) \qquad \ldots \qquad \ldots \quad (1)$$

and writing

$$b=2a-\alpha,$$

we find, by Elementary Geometry, that the feet of the three normals drawn to Σ from the corresponding centre of inversion D (α, β), are the three *finite* * points of intersection of Σ with the rectangular hyperbola (Ξ), viz.,

$$xy+by-2a\beta=0, \qquad \ldots \qquad \ldots \quad (2)$$

whose centre (L) is the point $(-b, 0)$, and whose asymptotes, viz.,

$$x+b=0 \text{ and } y=0$$

are identical, respectively with the *real* asymptote of the cubic Γ and the *common* axis of $\Sigma, \Sigma_1, \Sigma_2, \Sigma_3$.

* For brevity's sake, the expression *finite point* has been used to denote a point lying in the *finite* part of the plane, (as distinguished from a point lying on the line at infinity)

The *fourth* point of intersection of Σ and Ξ can be easily accounted for. For it is crystal-clear that, if K and K' be respectively the two points at infinity, attach

In view of (V) of Art 1, the equation (2) of Ξ can at pleasure be re-written in each of three (equivalent) forms :

$$xy+(2a_r-\alpha_r)y-2a_r\beta_r=0,\ (r=1,2,3). \qquad \ldots \quad (3)$$

Interpreting this result geometrically, and noting that *more than four* arbitrary points cannot—unless specially related to one another—lie upon one and the same rectangular hyperbola, we may summarise our conclusions in the following manner :—

For a bicursal circular cubic Γ, the sixteen special points, consisting of the four centres of inversion A, B, C, D and of the feet of the four triads of normals drawn from them respectively to the four focal parabolas $\Sigma_1, \Sigma_2, \Sigma_3, \Sigma$ must all lie on a certain rectangular hyperbola Ξ, whose asymptotes are respectively the real asymptote of Γ and the common axis of the four (confocal) focal parabolas.

Prior to the discussion of other geometrical features of the conic Ξ, we intend to make a short digression (in the next article) on the diverse types of polar conics of the original cubic Γ.

ing to the coordinate axes ($x=0$ and $y=0$), then (K, K') may as well be designated as the two points at infinity on Ξ. Remarkably, K is also the *real* point at infinity on Γ, (the other two points at infinity on Γ being the two circular points at infinity), whereas K' is the point of contact of Σ with the line at infinity. Thus this point K'—situated wholly at infinity—is the *fourth* point of intersection of Σ and Ξ, and is often ignored in the enumeration of points of intersection of the two conics. This explains the anomaly referred to.

According to (Euclidean) Projective Geometry, an *arbitrary* rt. line, lying in a plane, may *in a special sense* be said to be perpendicular to the line at infinity situated in that plane. The truth of this apparent paradox becomes manifest, if it is remembered that the condition of perpendicularity viz.

$$aa'+bb'=0$$

of two right lines, whose Cartesian equations are

$$ax+by+c=0 \quad \text{and} \quad a'x+b'y+c'=0$$

is fulfilled *independently* of a, b, if only $a'=0$, $b'=0$.

The afore-mentioned principle being borne in mind, it is clear that the line DK' is perpendicular to the line at infinity, which is, however, the tangent to Σ at K'. So DK' behaves like the normal to Σ at K'. This fourth normal (DK') from D to Σ being left out of consideration, we speak, as above, of only *three* (ordinary) normals (from D to Σ).

Art. 3. If $\phi(x, y)$ stands for the L.S of the equation (I) of Art. 1 the partial differential coefficients are given by

$$\left.\begin{array}{ll} \frac{\delta\phi}{\delta x}=3x^2+y^2+2bx+(c^2-4a\alpha); & \frac{\delta\phi}{\delta y}=2(xy+by-2a\beta), \\ \frac{\delta^2\phi}{\delta x^2}=2(3x+b); \quad \frac{\delta^2\phi}{\delta x\delta y}=2y; & \frac{\delta^2\phi}{\delta y^2}=2(x+b). \end{array}\right\}$$

We shall now invoke Art. 3 (Ch. VII, P. 93, Exs. 4, 6, 9) of Hilton's *Plane Algebraic Curves* (1919) to dispose of the sets of points, whose polar conics shall be of *prescribed* shapes.

Firstly the locus (Λ) of points, whose polar conics are rectangular hyperbolas, is a right line, whose equation is

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}=0, \text{ i.e., } x=-\frac{b}{2}. \qquad \ldots \quad (1)$$

Thus Λ is parallel to the real asymptote ($x=-b$) of the given cubic I.

Secondly, the locus (S) of points, whose polar conics are parabolas, is the hyperbola, whose equation is

$$\frac{\partial^2\phi}{\partial x^2}\frac{\partial^2\phi}{\partial y^2}-\left(\frac{\delta^2\phi}{\delta x\delta y}\right)^2=0, \text{ i.e., } (x+b)(3x+b)-y^2=0 \qquad \ldots \quad (2)$$

i.e.,
$$\frac{\left(x+\frac{2b}{3}\right)^2}{\left(\frac{b}{3}\right)^2}-\frac{y^2}{\left(\frac{b}{\sqrt{3}}\right)^2}=1.$$

So the centre of this hyperbola S is the point $M\left(-\frac{2b}{3}, 0\right)$ and its eccentricity is 2.

Thirdly, the polar conic will be a circle, if the coordinates of the point in question conform to both the relations

$$\frac{\delta^2\phi}{\delta x^2}=\frac{\delta^2\phi}{\delta y^2} \text{ and } \frac{\delta^2\phi}{\delta x\delta y}=0,$$

i.e., if the point coincides with the origin. That is to say, the double focus O (of Γ) represents the *only* point, whose polar conic (Γ) is a circle. This polar conic Γ—of *circular* shape—will afterwards be referred to as the *polar circle* of the given circular cubic Γ. The actual equation to Γ can be easily seen to be

$$b(x^2+y^2)+2\{(c^2-4a\alpha)x-4a\beta y\}+3\{2a(\alpha^2+\beta^2)-c^2\alpha\}=0, \qquad (3)$$

so that its centre (E) is the point

$$\left(\frac{c^2-4a\alpha}{b}, \frac{4a\beta}{b}\right), \qquad (4)$$

provided, of course, that $b\neq 0$ When, however, b o the polar circle breaks up into the line at infinity and an ordinary line

The symbol K being as before supposed to denote the *real* point at infinity on the given cubic Γ, and the symbol I representing the centre of the hyperbola Σ we shall now point out a sort of *reciprocal* relation between the points $O, E)$ and also between the points (K, L)

In the first place we remark that the polar conic of an arbitrary point (x, y) w r t Γ has for its Cartesian equation —

$$x\{3x^2+y^2+2bx+(c^2 \quad 4a\alpha)\}+2y(xy+by-2a\beta)$$
$$+[b(x^2+y^2)+2\{(c^2-4a\alpha)x-4a\beta y\}+3\{2a(\alpha^2+\beta^2)-c^2\alpha\}]=0 \qquad (5)$$

Accordingly the polar conic of the point E, as defined by (4), is given by

$$(c^2-4a\alpha)(3x^2+y^2)-b^2(x^2+y^2)-8a\beta xy=6ab(\alpha^2+\beta^2)$$
$$-3bc^2\alpha-(c^2-4a\alpha)^2-16a^2\beta^2,$$

which shews that the origin O is the centre

Next, by (5), the polar conic of the point L $(-b, o$ can be accommodated to the symbolic form

$$Ax^2+2Gx+2Fy+C \quad 0,$$

(where the co efficients are all constants) manifestly this conic is a parabola, which has its axis parallel to the real asymptote $(x \quad -b)$ of the cubic Γ, and which may, in the phraseology of Projective Geometry, be spoken of as a *special* type of central conic, the special feature being that its centre is situated at infinity and is none other than the real point K of Γ at infinity

To sum up the last set of results, we may simply state

(1) that the polar conic of any one of the two points (O, E) has the other for its centre,

and (ii) that the polar conic of any one of the two points (K, L) has the other for its centre.

Admittedly these results are to be regarded as simple illustrations of Casey's *general* principle that, whenever the polar conic of one point (w. r. t. a cubic) has another point for its centre, the polar conic of this latter point must have the former for its centre

The accompanying diagram exhibits roughly the relative positions of the several points and lines (last mentioned), intimately related to a bicursal circular cubic Γ, it being implied that the double focus O of Γ does *not* lie on the real asymptote (so that $b \quad 2a - \alpha \neq 0$)

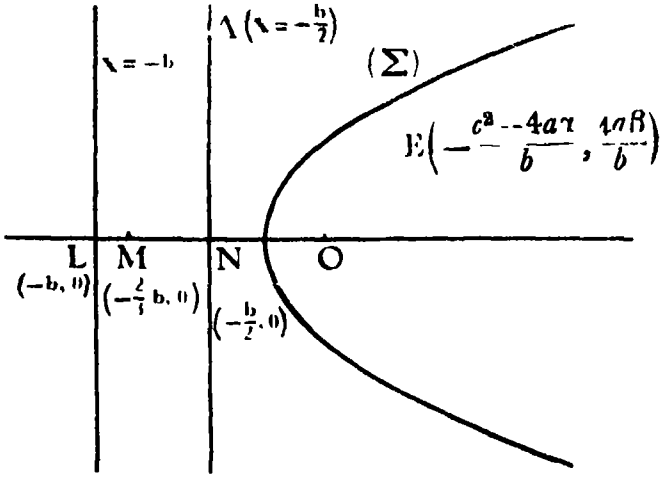


Fig. 1

In view of the results proved heretofore, the geometrical construction for the points L, M, N may be stated in the following *indirect* form:—

From the double focus O drop a perpendicular OL on the real asymptote of the given circular cubic Γ and bisect and trisect OL respectively at N and M, this latter point being the point of trisection nearer to the end-point L. Then the point L (i.e. the foot of the afore-said perpendicular) must be the centre of the rectangular hyperbola Ξ considered before. As for M, the characteristic property is that it is the centre of the hyperbola S, representing the locus of points, whose polar conics are parabolas. Finally, the point N has the distinctive property that the line, drawn through it parallel to the real asymptote of Γ, represents the locus of points, whose polar conics are rectangular hyperbolas.

The next article will be devoted to the consideration of the other type of circular cubic, whose double focus lies on its real asymptote, (so that $b = 2a - \alpha = 0$)

Art 4 Suppose that Γ is a circular cubic, whose double focus O lies on its real asymptote If I, J be the two circular points at infinity, and K denotes, as before the real point (of Γ) at infinity, the tangents at I, J, K must be concurrent, the point of concurrence being the double focus O (as shewn in Fig 2)

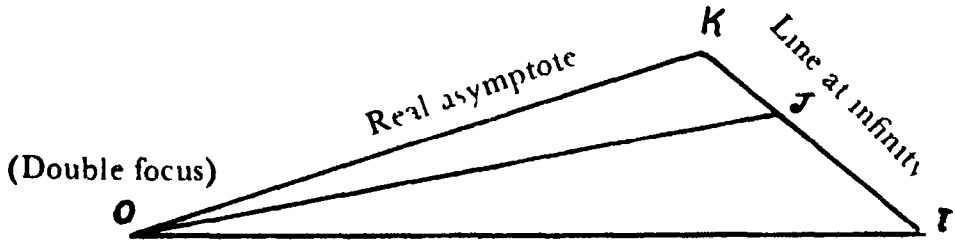


Fig 2

I, J, K, being the points of contact of three of the tangents, that can be drawn from O to Γ, must then lie on the polar conic of O Consequently the polar conic of O must consist of two right lines one of which is the line at infinity IJK The immediate inference is that the point O will lie on the Hessian (H) of Γ, and that the line at infinity will be a tangent to the Cayleyan

Hence, observing that, when b o, all the four points of Fig 1, viz, O, L, M, N, coincide, we can give the following garb to the final result —

A necessary condition for the double focus of a bicursal circular cubic Γ to lie on its real asymptote may be stated in any one of the following forms —

(*a*) *that the double focus should lie on the Hessian,*

(*b*) *that the double focus should lie on the line-locus of points, whose polar conics are rectangular hyperbolas,*

(*c*) *that the double focus should be the centre of the rectangular hyperbola* Ξ, *which passes through the four centres of inversion as also*

through the feet of the four triads of normals, drawn respectively from the four points to the four related focal parabolas;

(*d*) *that the double focus should be the centre of the hyperbola* (S), *which represents the locus of points, whose polar conics are parabolas;*

(*e*) *that the polar circle,* (*i e , the polar conic of the double focus*) *should break up into two right lines, one of which is the line at infinity;*

(*f*) *that the line at infinity should touch the Cayleyan of the cubic.*

It may not be out of place to remark that the class of bicursa circular cubics, having their double foci seated on their real asymptotes includes, within its fold, an important *sub-class*, consisting of *central* (and therefore bicursal) circular cubics. We observe incidentally that the converse of the property (*a*) is *not* necessarily true. In other words, when the double focus (of a bicursal circular cubic) lies on the Hessian, it may or may not lie on the real asymptote. The converse of each of the remaining properties (*b*), (*c*), (*d*), (*e*), (*f*) can be readily shown to be *valid*. That is to say, in order that the double focus of a bicursal circular cubic may lie on its real asymptote, the sets of conditions (*b*), (*c*), (*d*), (*e*), (*f*) are each necessary as well as sufficient, but the condition (*a*) is necessary, but by no means sufficient.

Art. 5. Let us now revert again to the *unrestricted* type of bicursal circular cubic Γ ($b \neq 0$). We now intend to establish another interesting property of the attached (rectangular) hyperbola Ξ.

It is common knowledge that, for a bicursal cubic Γ, the series of polar conics, answering to different points on a given right line W, constitute a *pencil*, passing through four *fixed* points, which are called the four *poles* of W. If we now look for the poles of the line at infinity *w. r. t.* the bicursal circular cubic Γ, given by (I) of Art. 1, we readily perceive that they are designable as the (four) points of intersection of the two conics:

$$\left.\begin{aligned} \frac{\partial\phi}{\partial x} &\equiv 3x^2+y^2+2bx+(c^2-4a\alpha)=0 \\ \text{and} \quad \frac{\partial\phi}{\partial y} &\equiv 2(xy+by-2a\beta)=0 \end{aligned}\right\}, \text{ where } \quad b=2a-\alpha\neq 0.$$

Reference to Art. 2 makes it plain that the second of the two conics is no else than the rectangular hyperbola Ξ. Because the first conic is an ellipse, it follows that Ξ is the *only* (†) rectangular hyperbola that can be drawn though the four poles.

We are therefore entitled to summarise our conclusions as under:—

The rectangular hyperbola Ξ, that passes through the four centres of inversion of a bicursal circular cubic Γ and also through the feet of the four triads of normals drawn from the four centres to their respective focal parabolas, may also at pleasure be characterised

(i) *as the uniquely determinate rectangular hyperbola that can pass through the four poles of the line at infinity,*

or (ii) *as the uniquely determinate polar conic, having the real asymptote of Γ for one of its own asymptotes.*

SECTION II.

Bicircular Quartics

Art 6. A bicursal bicircular quartic Γ possesses—in precisely the same way as a (bicursal) circular cubic does—four circles of inversion Π, Π_1, Π_2, Π_3 and four corresponding focal conics Σ, Σ_1, Σ_2, Σ_3, so

(†) Attending to the patent facts that the number of equilateral hyperbolas, that can be drawn through four *given* points, is either 1 or ∞, and that any one of the four centres of inversion is the orthocentre of the triangle-formed by the other three, one can easily explain why the rectangular hyperbola g is perfectly defined when it is said to pass through the four poles of the line at infinity, whereas the same curve (g) is *imperfectly* defined—defined (as a matter of fact) as one among *infinitely many* rectangular hyperbolas—when it is said to pass through the four centres of inversion.

related that Γ may be described as the envelope of the set of circles, havingtheir centres located on any one of the focal conics (say, Σ_r) and intersecting the associated circle Π_r at right angles. The analogy between the two cases is almost complete save as to the fact that, whereas each of the focal conics of a circular cubic is *non-central* (i.e., parabolic), the focal conics of a bicircular quartic are all *central* (i.e., elliptic or hyperbolic). If any of the circles of inversion (say, Π) and its attached focal conic Σ be taken in the respective Cartesian forms:

$$(x-\alpha)^2+(y-\beta)^2=k^2 \qquad \text{and} \qquad \frac{x^2}{a^2}+\frac{y^2}{b^2}=1, \quad \ldots \quad \ldots \qquad \text{(I)}$$

the equation to Γ is easily obtained in the form:

$$(x^2+y^2+c^2)^2=4\{a^2(x-\alpha)^2+b^2(y-\beta)^2\}, \quad \ldots \quad \ldots \qquad \text{(II)}$$

where $$c^2\equiv k^2-\alpha^2-\beta^2.$$

By elementary algebraic manipulations, (II) can be converted into each of the *equivalent* forms, viz.,

$$(x^2+y^2+C_r^2)^2=4\{a_r^2(x-\alpha_r)^2+b_r^2(y-\beta_r)^2\}, \qquad (r=1,2,3) \qquad \text{(III)}$$

provided that the new triads of constants

$$\{a_r\}\,,\ \{b_r\}\,,\ \{c_r\}\,,\ \{\alpha_r\}\,,\ \{\beta_r\}$$

are defined by

$$c_r^2=c^2+\lambda_r,\ a_r^2=a^2+\frac{\lambda_r}{2},\ b_r^2=b^2+\frac{\lambda_r}{2},\ \alpha_r=\frac{2a^2\alpha}{2a^2+\lambda_r},\ \beta_r=\frac{2b^2\beta}{2b^2+\lambda_r}, \qquad \text{(IV)}$$

and $\lambda_1, \lambda_2, \lambda_3$ are the three *non-zero* roots of the biquadratic in λ, viz.

$$\lambda^2+2c^2\lambda+4a^2\alpha^2+4b^2\beta^2-\frac{8a^4\alpha^2}{2a^2+\lambda}-\frac{8b^4\beta^2}{2b^2+\lambda}=0.$$

Comparison of the equations (II) and (III) at once points to the conclusion—which could be foreseen from other considerations—that the other three circles of inversion (Π_1, Π_2, Π_3) and the associated focal conics (Σ_1, Σ_2, Σ_3) are given by

$$(x-\alpha_r)^2+(y-\beta_r)^2=k_r^2 \ \text{and}\ \frac{x^2}{a_r^2}+\frac{y^2}{b_r^2}=1, \qquad (r=1,2,3)$$

it being understood that k_r is defined by

$$c_r^2=k_r^2-\alpha_r^2-\beta_r^2,$$

i.e., $$k_r^2=c^2+\lambda_r+\frac{4a^4\alpha^2}{(2a^2+\lambda_r)^2}+\frac{4b^4\beta^2}{(2b^2+\lambda_r)^2}.$$

We note here, for future reference, the following subsidiary relations (which follow automatically from IV or from a comparison of II and III):—

$$a_r^2 - b_r^2 = a^2 - b^2,$$

$$a_r^2\alpha_r = a^2\alpha \quad \text{and} \quad b_r^2\beta_r = b^2\beta, \ (r = 1, 2, 3). \qquad \ldots \quad (V)$$

Denoting the four centres of inversion (α, β), (α_1, β_1), (α_2, β_2), (α_3, β_3) by the letters D, A, B, C, we shall investigate (in the next article) the tetrads of normals that can be drawn from the four points to the corresponding focal conics Σ, Σ_1, Σ_2, Σ_3.

Art. 7. If we now pick out at random one of the focal conics (say, Σ) having for its Cartesian equation:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

we notice that the feet of the four normals, that can be drawn from the corresponding centre of inversion $D(\alpha, \beta)$ are the intersections of Σ, with the rectangular hyperbola Ξ, defined by

$$a^2\alpha y - b^2\beta x - (a^2 - b^2)xy = 0. \qquad \ldots \quad \ldots \quad \ldots \quad (1)$$

On the strength of (V) of Art. 6 the equation last written can be successively turned into the three *equivalent* forms:

$$a_r^2\alpha_r y - b_r^2\beta_r x - (a_r^2 - b_r^2)xy = 0. \qquad (r = 1, 2, 3). \qquad (2)$$

The obvious geometrical interpretation is that the sixteen points, viz., the feet of the four tetrads of normals, that can be drawn respectively from D, A, B, C, to the corresponding focal conics Σ, Σ_1, Σ_2, Σ_3 lie on one and the same rectangular hyperbola Ξ, which is completely definable by any one of the (equivalent) Cartesian equations (1), (2).

Regard being had to the undeniable fact that the hyperbola Ξ goes through the origin O, which is situated mid-way between the two real double foci $(\pm\sqrt{a^2 - b^2}, 0)$ of the quartic Γ, we can enunciate the final result in the undermentioned form:—

For a bicursal bicircular quartic Γ, the twenty special points, viz., the four centres of inversion, and the feet of the four tetrads of normals, drawn respectively from these centres to the four corresponding focal conics, lie on one

and the same rectangular hyperbola, whose asymptotes are respectively parallel and perpendicular to the line joining the two double foci of Γ, and which goes through the mid-point of this line.

SECTION III

(*Associated Differential Equations*)

Art. 8. A little reflection shows that, when a curve Γ of the most unrestricted type is given, there can, in general, be found an infinitude of *families* of curves, having Γ for their *common* envelope (complete or partial). Thus, for instance, the curve Γ is the envelope of:

(i)	its set of ∞^1 of tangents,					(if $n > 2$),
(ii)	,,	,,	,,	circles of double contact,		(if $n \geqslant 2$)
(iii)	,,	,,	,,	osculating circles,		(,,)
(iv)	,,	,,	,,	,,	parabolas,	(,,)
(v)	,,	,,	,,	,,	rectangular hyperbolas,	(,,)
(vi)	,,	,,	,,	,,	conics,	(if $n \geqslant 3$)
(vii)	,,	,,	,,	,,	cubics	(if $n \geqslant 4$)
(viii)	,,	,,	,,	,,	quartics,	(if $n \geqslant 5$)

and so forth.

It is abundantly clear that, if the general Cartesian equation of any of the above families of curves be taken in the functional form:

$$f(x, y, c) = 0, \quad \ldots \quad \ldots \quad (1)$$

the c-discriminant, say $F(x,y)$, when equated to zero and *freed from extraneous loci* (*if any*), will represent the original curve Γ. Furthermore, when the parameter c is eliminated from (1) by process of differentiation,

the resulting differential equation, viz: $\phi(x, y, p) = 0, \quad \left(p \equiv \frac{dy}{dx}\right) \ldots \quad (2)$

will have the same set of curves viz., (1) for its *integral curves*, and its p-discriminant, *freed* (*if need be*) *from extraneous loci*, will denote the original curve Γ. Thus *any given curve Γ may always be regarded as the*

common singular solution (complete or partial) of an infinite number of differential equations of the first order like (2).

In the succeeding article we shall illustrate the afore-mentioned principle with reference to a conic, a circular cubic and a bicircular quartic.

Art 9. There are a number of examples to be taken up one by one.

Example I. The parabola ($y^2=4ax$) is easily seen to be the *singular solution* of the differential equation:

$$(yp-2a)^2+y^2-4ax=0, \qquad \left(p\equiv\frac{dy}{dx}\right),$$

the general solution viz: $(x-t)^2+y^2-4ax=0$, (t is a parameter) representing the series of ∞^1 circles of double contact.

Example II. The ellipse: $\dfrac{x^2}{a^2}+\dfrac{y^2}{b^2}=1$

is the *common* singular solution of the two differential equations viz.,:

$$\left.\begin{aligned}&\left(\frac{py}{b^2}+\frac{x}{a^2}\right)^2-\left(\frac{1}{a^2}-\frac{1}{b^2}\right)\left(\frac{x^2}{a^2}+\frac{y^2}{b^2}-1\right)=0,\\ \text{and}\quad &\left(\frac{1}{p}\frac{x}{a^2}+\frac{y}{b^2}\right)^2-\left(\frac{1}{b^2}-\frac{1}{a^2}\right)\left(\frac{x^2}{a^2}+\frac{y^2}{b^2}-1\right)=0,\end{aligned}\right\}\quad\left(p\equiv\frac{dy}{dx}\right),$$

their respective *general* solutious, viz:

$$\left.\begin{aligned}&\frac{x^2}{a^2}+\frac{y^2}{b^2}-1-\left(\frac{1}{a^2}-\frac{1}{b^2}\right)(x-t)^2=0,\\ \text{and}\quad &\frac{x^2}{a^2}+\frac{y^2}{b^2}-1-\left(\frac{1}{b^2}-\frac{1}{a^2}\right)(y-t)^2=0,\end{aligned}\right\}\ (t \text{ is a parameter})$$

representing the two systems of circles of double contact that the conic can have. Evidently the corresponding result for a hyperbola is to be deduced by changing b^2 into $-b^2$.

Example III. For a bicursal circular cubic Γ, we may proceed as in Art. 1, and represent a circle of inversion π and its related focal parabola Σ in the respective forms:

$$(x-\alpha)^2+(y-\beta)^2=k^2 \qquad \text{and} \qquad y^2=4a(x+a)$$

and finally derive the equation of Γ in the symbolic form :

$$(x-\alpha)S+2a(y-\beta)^2=a, \quad \ldots \quad \ldots \quad \ldots \quad (A)$$

where $$S=x^2+y^2+2ax+c^2-2a\alpha$$

and $$c^2=k^2-\alpha^2-\beta^2.$$

Manifestly the family of circles, whose centres lie on Σ and which cut π orthogonally, has for its *functional equation:*

$$2at^2(x-a)-4at(y-\beta)-S=0, \quad \text{(where } t \text{ is a parameter)} \quad \ldots \quad (B)$$

The *associated* differential equation is readily seen to be

$$\{S-2(x-\alpha)(x+py+a)\}^2-8a\{p(x-\alpha)-(y-\beta)\}$$
$$\{pS-2(y-\beta)(x+py+a)\}=0, \quad \ldots \quad (C)$$

where $$p=\frac{dy}{dx}$$

Accordingly, this differential equation has (B) for its *general* solution, and (A) for its *singular* solution

Repeating the same line of argument, we infer that the other three differential equations (of the first order), which claim in common with (C), the original bicursal cubic Γ, viz, (A) for a *common* singular solution, are of the type :

$$\{S_r-2(x-\alpha_r)(x+py+a_r)\}^2-8a_r\{p(x-\alpha_r)-(y-\beta_r)\}$$
$$\{pS_r-2(y-\beta_r)(x+py+a_r)\}=0 \quad (r=1, 2, 3,),$$

it being understood that

$$a_r=a+\lambda_r,\ \alpha_r=\alpha+2\lambda_r,\ \beta_r=\frac{a\beta}{a+\lambda_r}, \quad c_r^2=c^2+4\lambda_r(2a+\alpha)+8\lambda_r^2,$$
$$S_r=x^2+y^2+2a_rx+c_r^2-2a_r\alpha_r,$$

and that $\lambda_1, \lambda_2, \lambda_3$ are the three *non-zero* roots of

$$\frac{a^2\beta^2}{a+\lambda}+(a \quad \lambda)(a+2\lambda)^2-4a\lambda(\alpha+2\lambda)-c^2\lambda-a(\alpha^2+\beta^2)=0$$

It goes without saying that the corresponding *general solutions* are to be deduced from (B) by changing a, α, β, c, S respectively into $a_r, \alpha_r, \beta_r, c_r, S_r$.

Example IV The equation of a bicursal bicircular quartic Γ being, as in Art. 5, taken in the form:

$$(x^2+y^2+c^2)^2=4\{a^2(x-\alpha)^2+b^2(y-\beta)^2\}, \ (c^2=k^2-\alpha^2-\beta^2), \quad (I)$$

where of course, a circle of inversion π and the related focal conic Σ are given by

$$(x-\alpha)^2+(y-\beta)^2=k^2 \qquad \text{and} \qquad \frac{x^2}{a^2}+\frac{y^2}{b^2}=1,$$

it is easy to verify that the *functional equation* of the series of circles of double contact having their centres located on Σ, is

$$2a(x-\alpha)\cos t+2b(y-\beta)\sin t-(x^2+y^2+c^2)=0, \ (t \text{ is a parameter}) \qquad \ldots \text{(II)}$$

whereas the corresponding *differential equation* is

$$a^2\{(x^2+y^2+c^2)-2(x-\alpha)(x+py)\}^2+b^2\{p(x^2+y^2+c^2)-2(y-\beta)(x+py)\}^2$$
$$-4a^2b^2\{p(x-\alpha)-(y-\beta)\}^2=0, \ \left(p \ \frac{dy}{dx}\right). \qquad \ldots \text{(III)}$$

In other words, the bicircular quartic Γ, as given by (I) is the singular solution of (III), the general solution being, of course, (II)

Evidently the other three differential equations of the type (III) having (I) for their *common* singular solution, are given by

$$a_r^2\{(x^2+y^2+c_r^2)^2-2(x-\alpha_r)(x+py)\}^2+b_r^2\{p(x^2+y^2+c_r^2)-2(y-\beta_r)(x+py)\}^2$$
$$-4a_r^2b_r^2\{p(x-\alpha_r)-(y-\beta_r)\}^2=0, \ \left(p\equiv\frac{dy}{dx}\right), \qquad \text{(IV)}$$

it being postulated that $\{a_r\}$, $\{b_r\}$, $\{c_r\}$, $\{\alpha_r\}$ and $\{\beta_r\}$ are defined by

$$a_r^2 \quad a^2+\frac{\lambda_r}{2}, \quad b_r^2-b^2+\frac{\lambda_r}{2}, \quad c_r^2-c^2+\lambda_r$$
$$\alpha_r=\frac{2a^2\alpha}{2a^2+\lambda_r} \quad \beta_r \quad \frac{2b^2\beta}{2b^2+\lambda_r},$$

and λ_1, λ_2, λ_3 are the three *non-zero* roots of the biquadratic in λ, viz,

$$\lambda^2+2c^2\lambda+4a^2\alpha^2+4b^2\beta^2-\frac{8a^4\alpha^2}{2a^2+\lambda}-\frac{8b^4\beta^2}{2b^2+\lambda}=0.$$

Needless to say, the *general* solutions of the three differential equations of the category (IV) are derivable from (II) by changing

$$a, b, c, \alpha, \beta$$

respectively into $\qquad a_r, b_r \ c_r, \alpha_r, \beta_r.$

Thus, as is to be expected, the general solutions of the four differential equations (III) and (IV) are quite *distinct* from one another although their *singular solution* is the same.

It is hardly necessary to mention that in each of the four examples I—IV, considered in this section, the singular solution represents only the envelope, there being no extraneous locus included in it.

MOTION IN FLUIDS OF VARIABLE DENSITY AND VARYING COEFFICIENT OF VISCOSITY

By

SANTI RAM MUKHERJEE

(Engineering College Banaras Hindu University)

Received on 2nd April 1948

This paper is in continuation with the auther's previous papers already published in the Proc edings of the National Academy of Sciences, India In the previous papers motion in incompressible fluid either with varying coefficient of viscosity or variable density has been investigated Here motion when both density and viscosity vary at the same tim , has been studied We have treated here both of them as linearly varying and assumed $\rho = \rho_0 + \lambda x$ and $\mu = \mu_0 \epsilon x$, where ρ_0 and μ_0 are the the values of ρ and μ respectively at the origin and λ and ϵ are constants Here λ is a small quantity of the first order but ϵ not necessarily too small to be neglected

The formula of stokes [1] for the resistance experienced by a slowly moving sphere in a fluid of constant density has been employed in physical researches of fundamental importance, as a means of estimating the size of minute globules of water and thence the number of globules contained in a cloud of given mass, and has led to much discussi n both from the experimental and from the theoretical side Ose n made a i interesting innovation in the treatment of the above problem

Here we have discussed the slow and steady motion, in the manner of Oseen, and solutions of hydrodynamical equations arising out of motion have been obtained in series

Assuming the above laws of variati n in ρ and μ and neglecting extraneous forces, the equa ions of motion are, in the method of Oseen,

$$\left.\begin{aligned}
(\rho_0+\lambda x)U\frac{\partial u}{\partial x} &= -\frac{\partial p}{\partial x}+(\mu_0+\varepsilon x)\ \nabla^2 u+\varepsilon\left(\frac{\partial u}{\partial x}+\frac{\partial u}{\partial x}\right)-\frac{2}{3}\epsilon\left(\frac{u\partial}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)\\
(\rho_0+\lambda x)U\frac{\partial v}{\partial x} &= -\frac{\partial p}{\partial y}+(\mu_0+\varepsilon x)\ \nabla^2 v+\varepsilon\left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right)\\
(\rho_0+\lambda x)U\frac{\partial w}{\partial x} &= -\frac{\partial p}{\partial z}+(\mu_0+\varepsilon x)\ \nabla^2 u+\varepsilon\left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)\\
&\text{with the equation of continuity}\\
&\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=-\frac{U\lambda}{\rho_0}
\end{aligned}\right\}(1)$$

by writing $U+u$ for u and neglecting small quantities of the second order. These latter symbols now denote the components of the velocity which would remain if a translation $-U$ were superposed on the whole system. Putting $\bar{u}=u+\frac{U\lambda}{\rho_0}x$ in (1) we have

$$\left.\begin{aligned}
&(\rho_0+\lambda x)U\frac{\partial \bar{u}}{\partial x}=-\frac{\partial p}{\partial x}+(\mu_0+\varepsilon x)\ \nabla^2\bar{u}+\varepsilon\left(\frac{\partial \bar{u}}{\partial x}+\frac{\partial u}{\partial x}\right)+\\
&(\rho_0+\lambda x)U\frac{U\lambda}{\rho_0}-\frac{2\varepsilon U\lambda}{\rho_0}+\frac{2\epsilon U\lambda}{3\rho_0}\\
&(\rho_0+\lambda x)U\frac{\partial v}{\partial x}=-\frac{\partial p}{\partial y}+(\mu_0+\varepsilon x)\ \nabla^2 v+\varepsilon\left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right)\\
&(\rho_0+\lambda x)U\frac{\partial w}{\partial x}=-\frac{\partial p}{\partial z}+(\mu_0+\varepsilon x)\ \nabla^2 w+\varepsilon\left(\frac{\partial w}{\partial z}+\frac{\partial u}{\partial z}\right)\\
&\text{with}\quad \theta\equiv\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=0.
\end{aligned}\right\}\ ..(1a)$$

Let $u=u_1+u_2$, $v=v_1+v_2$ and $w=w_1+w_2$ such that

$$\left.\begin{aligned}
&(\rho_0+\lambda x)U\frac{\partial \bar{u}_1}{\partial x}+\lambda U u_1-\varepsilon\left(\frac{\partial u_1}{\partial x}+\frac{\partial \bar{u}_1}{\partial x}\right)=-\frac{\partial p}{\partial x}+(\mu_0+\varepsilon x)\nabla^2 u_1\\
&(\rho_0+\lambda x)U\frac{\partial v_1}{\partial x}-\varepsilon\left(\frac{\partial v_1}{\partial x}+\frac{\partial u_1}{\partial y}\right)=-\frac{\partial p}{\partial y}+(\mu_0+\varepsilon x)\nabla^2 v_1\\
&(\rho_0+\lambda x)U\frac{\partial w_1}{\partial x}-\varepsilon\left(\frac{\partial w_1}{\partial x}+\frac{\partial \bar{u}_1}{\partial z}\right)=-\frac{\partial p}{\partial z}+(\mu_0+\varepsilon x)\nabla^2 w_1\\
&\text{with}\quad \theta_1\equiv\frac{\partial \bar{u}_1}{\partial x}+\frac{\partial v_1}{\partial y}+\frac{\partial w_1}{\partial z}=0
\end{aligned}\right\}..(2)$$

and

$$(\rho_0+\lambda x)\,U\frac{\partial \bar{u}_2}{\partial x}-\lambda\,U\mu_1-\varepsilon\left(\frac{\partial \bar{u}_2}{\partial x}+\frac{\partial \bar{u}_2}{\partial x}\right)=(\mu_0+\varepsilon x)\,\nabla^2\bar{u}_2+\frac{U\lambda}{\rho_0}\{(\rho_0+\lambda x)U-\tfrac{4}{3}\}$$

$$(\rho_0+\lambda x)\,U\frac{\partial v_2}{\partial x}\qquad -\varepsilon\left(\frac{\partial v_2}{\partial x}+\frac{\partial \bar{u}_2}{\partial y}\right)=(\mu_0+\varepsilon x)\,\nabla^2 v_2$$

$$(\rho_0+\lambda x)\,U\frac{\partial w_2}{\partial x}\qquad -\varepsilon\left(\frac{\partial w_2}{\partial x}+\frac{\partial u_2}{\partial z}\right)=\mu\quad+\varepsilon x)\,\nabla^2 w_2$$

with $\theta_2=\frac{\partial \bar{u}_2}{\partial x}+\frac{\partial v_2}{\partial y}+\frac{\partial w_2}{\partial z}=0.$

If there be a velocity potential ϕ such that $u_1=\frac{\partial \bar{\phi}}{\partial x}, v_1=\frac{\partial \phi}{\partial y}$ & $w_1=\frac{\partial \bar{\phi}}{\partial z}$ the equations in (2) are modified to

$$\left.\begin{aligned}
&(\rho_0+\lambda x)U\frac{\partial \bar{u}_1}{\partial x}+\lambda U\bar{u}_1-\varepsilon\left(\frac{\partial u_1}{\partial x}+\frac{\partial u_1}{\partial x}\right)=-\frac{\partial p}{\partial x}\\
&(\rho_0+\lambda x)U\frac{\partial v_1}{\partial x}\qquad -\varepsilon\left(\frac{\partial v_1}{\partial x}+\frac{\partial u_1}{\partial y}\right)=-\frac{\partial p}{\partial y}\\
&(\rho_0+\lambda x)U\frac{\partial w_1}{\partial x}\qquad -\varepsilon\left(\frac{\partial w_1}{\partial z}+\frac{\partial \bar{u}_1}{\partial z}\right)=-\frac{\partial p}{\partial x}\\
&\text{with } \nabla^2\bar{\phi}=0
\end{aligned}\right\}\quad\cdots\quad(4)$$

provided $$p=\{(\rho_0+\lambda x)\,U-2\varepsilon\}\frac{\partial \phi}{\partial x}.\qquad\cdots\quad(5)$$

(3) may be put in the form

$$\left.\begin{aligned}
&(\mu_0+\varepsilon x)\,\nabla^2\bar{u}_2-\{(\rho_0+\lambda x)U\quad\varepsilon\}\frac{\partial \bar{u}_2}{\partial x}+\varepsilon\frac{\partial \bar{u}_2}{\partial x}=-\lambda U\bar{u}_1-\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\frac{U\lambda}{\rho_0}\{(\rho_0+\lambda x)U-\tfrac{1}{3}\epsilon\}\\
&(\mu_0+\varepsilon x)\,\nabla^2 v_2-\{(\rho_0+\lambda x)U-\varepsilon\}\frac{\partial v_2}{\partial x}+\varepsilon\frac{\partial \bar{u}_2}{\partial y}=0\\
&(\mu_0+\varepsilon x)\,\nabla^2 w_2-\{(\rho_0+\lambda x)U-\varepsilon\}\frac{\partial w_2}{\partial x}+\varepsilon\frac{\partial \bar{u}_2}{\partial z}=0\\
&\text{with } \theta_2=0.
\end{aligned}\right\}\cdots(3a)$$

Since the vortex lines must be circles having the axis of x as a common axis, we may assume

$$\xi=0,\ \eta=-\frac{\partial \chi}{\partial z}\ \text{and}\ \zeta=\frac{\partial \chi}{\partial y}\qquad\cdots\quad(6)$$

Using $\xi = \frac{\partial w_2}{\partial y} - \frac{\partial v_2}{\partial z}$, $\eta = \frac{\partial \bar{u}_2}{\partial z} - \frac{\partial w_2}{\partial x}$ and $\zeta = \frac{\partial v_2}{\partial x} - \frac{\partial \bar{u}_2}{\partial y}$ and after necessary modifications we get

$$\left.\begin{aligned}\left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U-\varepsilon\right\}\frac{\partial}{\partial x}\right]\eta &= \varepsilon\nabla^2 w_2 - \lambda U\frac{\partial w_2}{\partial x} - \lambda U\frac{\partial \bar{u}_1}{\partial z}\\ \left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U-\varepsilon\right\}\frac{\partial}{\partial x}\right]\zeta &= -\varepsilon\nabla^2 v_2 + \lambda U\frac{\partial v_2}{\partial x} + \lambda U\frac{\partial \bar{u}_1}{\partial y}\end{aligned}\right\} \quad (7)$$

Again, since $\theta_2 = 0$,

$$\left.\begin{aligned}\frac{\partial \eta}{\partial z} - \frac{\partial \zeta}{\partial y} &= \nabla^2 u_2\\ \frac{\partial \zeta}{\partial x} - \frac{\partial \xi}{\partial z} &= \nabla^2 v_2\\ \text{and}\quad \frac{\partial \xi}{\partial y} - \frac{\partial \eta}{\partial x} &= \nabla^2 w_2\end{aligned}\right\}, \text{ we get (7)}$$

to be

$$\left.\begin{aligned}\left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x}\right]\eta &= -\lambda U\frac{\partial w_2}{\partial x} - \lambda U\frac{\partial u_1}{\partial z}\\ \left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x}\right]\zeta &= -\lambda U\frac{\partial v_2}{\partial x} + \lambda U\frac{\partial u_1}{\partial y}\end{aligned}\right\} \quad (7a)$$

since $\xi = 0$.

(7*a*) may again be simplified to the form

$$\left.\begin{aligned}\left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x} - \lambda U\right]\eta &= -\lambda U\left(\frac{\partial u_2}{\partial z} + \frac{\partial \bar{u}_1}{\partial y}\right)\\ \left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x} - \lambda U\right]\zeta &= \lambda U\left(\frac{\partial \bar{u}_2}{\partial y} + \frac{\partial \bar{u}_1}{\partial y}\right)\end{aligned}\right\} \quad (7b)$$

From 7(*b*) we get

$$\left[(\mu_0+\varepsilon x)\nabla^2 - \left\{(\rho_0+\lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x} - \lambda U\right]\chi = \lambda U(u_1+\bar{u}_2)$$
$$= \lambda U\bar{u} \quad \ldots \quad (8)$$

an additive function of x be ng obviously irrelevant

Turning back to (3*a*) we have

$$\left\{(\rho_0+\lambda x)U - \varepsilon\right\}\frac{\partial v_2}{\partial x} = (\mu_0+\varepsilon x)\nabla^2 v_2 + \varepsilon\frac{\partial u_2}{\partial y}$$

$$= (\mu + \varepsilon x)\frac{\partial^2 \chi}{\partial x \partial y} + \varepsilon \frac{\partial v_2}{\partial x} - \varepsilon \zeta$$

$$\text{or } \left\{(\rho + \lambda x)U - 2\varepsilon\right\}\frac{\partial v_2}{\partial x} = \mu + \varepsilon x \frac{\partial \chi}{\partial x \partial y} + \frac{\partial \chi}{\partial y} - 2\varepsilon \frac{\partial \chi}{\partial y}$$

$$\text{or } \frac{\partial v_2}{\partial x} = \frac{1}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial}{\partial x}\left\{(\mu + \varepsilon x)\frac{\partial \chi}{\partial y}\right\} - \frac{\mu}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial \chi}{\partial y}$$

$$\left.\begin{aligned} \text{so that } v_2 &= \frac{\mu + \varepsilon x}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial \chi}{\partial y} - \lambda U \int \frac{\mu + \varepsilon x}{\{(\rho + \lambda x)U - 2\varepsilon\}^2}\frac{\partial \chi}{\partial y}dx \\ &\quad - 2\varepsilon \int \frac{1}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial \chi}{\partial y}dx \\ \text{And } w_2 &= \frac{\mu + \varepsilon x}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial \chi}{\partial z} + \lambda U \int \frac{\mu + \varepsilon x}{\{(\rho + \lambda x)U - 2\varepsilon\}^2}\frac{\partial \chi}{\partial z}dx \\ &\quad - 2\varepsilon \int \frac{1}{(\rho + \lambda x)U - 2\varepsilon}\frac{\partial \chi}{\partial z}dx \end{aligned}\right\} \quad (9)$$

Now we have to determine χ to find u, v and u_2. From 8 we get

$$\left[(\mu_0 + \varepsilon x)\nabla^2 - \left\{(\rho + \lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x}\right] \times$$

$$\left[(\mu + \varepsilon x)\nabla - \left\{(\rho + \lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x} - \lambda U\right]\chi = \lambda U \frac{\partial p}{\partial x}, \text{ by } (1a)$$

$$= \lambda U\left[\left\{(\rho + \lambda x)U - 2\varepsilon\right\}\frac{\partial}{\partial x} + \lambda U \frac{\partial}{\partial x}\right], \text{ by } (5) \qquad (10)$$

Turning to the solution of the above equation we observe that since the problem is one of preferential motion along the axis of x we are justified in considering the solution of $\nabla^2\phi = 0$ in the form $\phi = R\,S$ where R is a function of x only and S that of ω and ϕ only where $\omega = \sqrt{y^2 + z^2}$ and $\tan\phi = \frac{z}{y}$, so that from $\nabla^2\phi = 0$ we get $\frac{1}{R}\frac{dR}{dx} + \frac{1}{S}\nabla_1 S = 0$ where $\nabla^2 = \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. This is satisfied if we write

$\frac{d^2R}{dx^2} - kR = 0$ and $\nabla_1 S + kS = 0$ where k is an arbitrary constant. These give $R = c_1 e^{\sqrt{k}x} + c_2 e^{-\sqrt{k}x}$, c_1 and c_2 being arbitrary constants, and

$$S = \sum A_n J_n(\beta_1 \omega)\left\{\begin{matrix}\cos \\ \sin\end{matrix}\right\} n\phi, \text{ if } k = \beta_1^2$$

$$\text{or } B_m I_m(\beta_2 w) \left.\begin{matrix}\cos\\ \sin\end{matrix}\right\} m\phi, \text{ if } k=-\beta_2^2.$$

In the differential equation (10) put $\chi = VS$ where V is a function of x only, so that

$$\left[(\mu_0+\varepsilon x)\nabla^2-\{(\rho_0+\lambda x)U-2\varepsilon\}\frac{\partial}{\partial x}\right]\left[(\mu_0+\varepsilon x)\left(\frac{d^2V}{dx^2}-kV\right)\right.$$
$$\left.-\{(\rho_0+\lambda x)U-2\varepsilon\}\frac{dV}{dx}-\lambda UV\right]S$$
$$=\lambda U\left[\{(\rho_0+\lambda x)U-2\varepsilon\}\frac{d^2R}{dx^2}+\lambda U\frac{dR}{dx}\right]S$$

Further simplification leads to

$$(\mu_0+\varepsilon x)^2\frac{d^4V}{dx^4}-2(\mu_0+\varepsilon x)\{(\rho_0+\lambda x)U-3\varepsilon\}\frac{d^3V}{dx^3}-$$
$$\left[2k(\mu_0+\varepsilon x)^2+3\lambda U(\mu_0+\varepsilon x)-\{(\rho_0+\lambda x)U-2\varepsilon\}\{(\rho_0+\lambda x)U-3\varepsilon\}\right]\frac{d^2V}{dx^2}$$
$$+\left[2k(\mu_0+\varepsilon x)\{(\rho_0+\lambda x)U-3\varepsilon\}+2\lambda U\{(\rho_0+\lambda x)U-2\varepsilon\}\right]\frac{dV}{dx}$$
$$+\left[k^2(\mu_0+\varepsilon x)^2+k\lambda U(\mu_0+\varepsilon x)+6k\{(\rho_0+\lambda x)U-2\varepsilon\}\right]V$$
$$-\lambda U\left[\lambda U\frac{dR}{dx}-k\{(\rho_0+\lambda x)U-2\varepsilon\}R\right] \quad . \quad . \qquad (11)$$

Putting $\mu_0+\varepsilon x=\varepsilon x_1$, $\rho_0/\varepsilon=\rho_1$, $\lambda/\varepsilon=\lambda_1$, $\mu_0/\varepsilon=\mu_1$ and thus $\rho_1+\lambda_1 x=\rho_1-\lambda_1\mu_1+\lambda_1 x_1=\rho_2+\lambda_1 x_1$ (say), in (11) we get

$$x_1^2\frac{d^4V}{dx_1^4}-2x_1\{\lambda_1 Ux_1+(\rho_2U-3)\}\frac{d^3V}{dx_1^3}$$
$$+\left[(\lambda_1^2U^2-2k)x_1^2+\lambda_1U(2\rho_2U-5-3)x_1+\rho_2^2U^2-5\rho_2U+6\right]\frac{d^2V}{dx_1^2}$$
$$+2\left[k\lambda_1Ux_1^2+(k\rho_2U-3k+\lambda_1^2U^2)x_1+\lambda_1U(\rho_2U-2)\right]\frac{dV}{dx_1}$$
$$+k\left[kx_1^2+2\lambda_1Ux_1+(\rho_2U-2)\right]V=\lambda_1U\left[\lambda_1U\frac{dR}{dx_1}-k\{\lambda_1Ux_1+(\rho_2U-2)\}R\right]$$
$$=R^{x_1}\text{ (say)} \quad . \quad . \quad . \quad (12)$$

First let us solve

$$x_1^2\frac{d^4V}{dx_1^4}-2x_1\left\{\lambda_1Ux_1+\rho_2U-3)\right\}\frac{d^3V}{dx_1^3}$$
$$+\left\{(\lambda_1^2U^2-2k\ x_1\ +2\lambda_1U\ \rho_2U-4)x_1+(\rho_2U)-2\ (\rho_2U-3)\right\}\frac{d^2V}{dx_1^2}$$
$$2\left[k\lambda_1Ux_1^2+\{\lambda_1\ U^2+k\ \rho_2U-3)\}x_1+\lambda_1U\ \rho_2U-2)\right]\frac{dV}{dx_1}$$
$$+k\left\{kx_1^2+2\lambda_1U\ x_1+\ \rho_2U-2)\right\}V=0 \qquad . \quad (13)$$

or $D_1V=0$, where D_1 Stands for the operator of V

Construct an expression of the form

$$W=\sum_{n=}^{n}c_n\,x_1^{\alpha+n}$$

$$D_1W-\Sigma c_0\,[\alpha(\alpha-1)\{(\alpha-2)(\alpha-3)-2(\alpha-2)(\rho_2U-3)$$
$$+(\rho_2U-2)(\rho_2U-3)\}x_1^{\alpha}$$
$$+\alpha x_1^{\alpha-1}\{-2\lambda_1U(\alpha-1)(\alpha-2)+2\lambda_1U(\rho_2U-1)(\alpha-1$$
$$+2\lambda_1U(\rho_2U-2)\}$$
$$+x_1^{\alpha}\{\alpha(\alpha-1)(\lambda_1^2U^2-2k)+2\alpha(\lambda_1^2U^2+k\ \rho_2U-3)$$
$$+k(\rho_2U-2)\}$$
$$+x_1^{\alpha+1}\ 2k\lambda_1U\ (\alpha+1)+k^2x_1^{\alpha+2}\ ]$$

ut $f_1=\lambda_1^2U^2-2k$, $f_2=2(\lambda_1^2U^2+k\ \rho_2U-3)$ and $f_3\quad k\ \rho_2U-2)$,

so that

$$D_1W=c_0[\alpha(\alpha-1)(\alpha-\rho_2U)(\alpha+1-\rho_2U)x_1^{\alpha-2}-2\lambda_1U\ \alpha^2(\alpha+1-\rho_2U)x_1^{\alpha-1}$$
$$+\{f_1\alpha(\alpha-1)+f_2\alpha+f_3\}x_1^{\alpha}+2k\lambda_1U\ (\alpha+1)x_1^{\alpha+1}+k^2x_1^{\alpha+2}]$$
$$c_1[(\alpha+1)\alpha(\alpha+1-\rho_2U)(\alpha+2-\rho_2U)x_1^{\alpha-1}-2\lambda_1U\ (\alpha+1)^2(\alpha+$$
$$2-\rho_2U)x_1^{\alpha}+\{f_1(\alpha+1)\alpha+f_2(\alpha+1)+f_3\}x_1^{\alpha+1}$$
$$+2k\lambda_1U(\alpha+2)x_1^{\alpha+2}+k^2x_1^{\alpha+3}\ ]$$
$$c_2[(\alpha+2)(\alpha+1)(\alpha+2-\rho_2U)(\alpha+3-\rho_2U)\ x_1^{\alpha}-2\lambda_1U\ (\alpha+2)^2(\alpha$$
$$-\rho_2U)x_1^{\alpha+1}+\{f_1(\alpha+2)(\alpha+1)+f(\alpha+2)+f_3\}x_1^{\alpha+2}$$
$$+2k\lambda_1U(\alpha+3)x_1^{\alpha+3}+k^2x_1^{\alpha+4}\ ]$$
$$c_3[(\alpha+3)(\alpha+2)(\alpha+3-\rho_2U)(\alpha+4-\rho_2U)x_1^{\alpha+1}-2\lambda_1U\ (\alpha+3)^2(\alpha+$$
$$-\rho_2U)x_1^{\alpha+2}+\{f_1(\alpha+3)(\alpha+2)+f_2(\alpha+3)+f\}x_1^{\alpha+3}$$
$$+2k\lambda_1U\ (\alpha+4)x_1^{\alpha+4}+k^2x_1^{\alpha+5}]$$

$$+ \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad +$$

$$+c_{n-2}[(\alpha+n-2)(\alpha+n-3)(\alpha+n-2-\rho_2 U)(\alpha+n-1-\rho_2 U)x_1^{\alpha+n-4}-2\lambda_1 U(\alpha+n-2)^2(\alpha+n-1-\rho_2 U)x_1^{\alpha+n-3}+\{f_1(\alpha+n-2)(\alpha+n-3)+f_2(\alpha+n-2)+f_3\}x_1^{\alpha+n-2}+2k\lambda_1 U(\alpha+n-1)x_1^{\alpha+n-1}+k^2x_1^{\alpha+n}]$$

$$+c_{n-1}[(\alpha+n-1)(\alpha+n-2)(\alpha+n-1-\rho_2 U)(\alpha+n-\rho_2 U)x_1^{\alpha+n-3}-2\lambda_1 U(\alpha+n-1)^2(\alpha+n-\rho_2 U)x_1^{\alpha+n-2}+\{f_1(\alpha+n-1)(\alpha+n-2)+f_2(\alpha+n-1)+f_3\}x_1^{\alpha+n-1}+2k\lambda_1 U(\alpha+n)x_1^{\alpha+n}+k^2x_1^{\alpha+n+1}]$$

$$+c_n[(\alpha+n)(\alpha+n-1)(\alpha+n-\rho_2 U)(\alpha+n+1-\rho_2 U)x_1^{\alpha+n-2}-2\lambda_1 U(\alpha+n)^2(\alpha+n+1-\rho_2 U)x_1^{\alpha+n-1}+\{f_1(\alpha+n)(\alpha+n-1)+f_2(\alpha+n)+f_3\}x_1^{\alpha+n}+2k\lambda_1 U(\alpha+n+1)x_1^{\alpha+n+1}+k^2x_1^{\alpha+n+2}]$$

$$+c_{n+1}[(\alpha+n+1)(\alpha+n)(\alpha+n+1-\rho_2 U)(\alpha+n+2-\rho_2 U)x_1^{\alpha+n-1}-2\lambda_1 U(\alpha+n+1)^2(\alpha+n+2-\rho_2 U)x_1^{\alpha+n}+\{f_1(\alpha+n+1)(\alpha+n)+f_2(\alpha+n+1)+f_3\}x_1^{\alpha+n+1}+2k\lambda_1 U(\alpha+n+2)x_1^{\alpha+n+2}+k^2x_1^{\alpha+n+3}]$$

$$+c_{n+2}[(\alpha+n+2)(\alpha+n+1)(\alpha+n+2-\rho_2 U)(\alpha+n+3-\rho_2 U)x_1^{\alpha+n}-2\lambda_1 U(\alpha+n+2)^2(\alpha+n+3-\rho_2 U)x_1^{\alpha+n+1}+\{f_1(\alpha+n+2)(\alpha+n+1)+f_2(\alpha+n+2)+f_3\}x_1^{\alpha+n+2}+2k\lambda_1 U(\alpha+n+3)x_1^{\alpha+n+3}+k^2x_1^{\alpha+n+4}]$$

$$+ \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad + \quad . \quad . \quad . \quad +$$

Thus $D_1W = c_0\alpha(\alpha-1)(\alpha-\rho_2 U)(\alpha+1-\rho_2 U)x_1^{\alpha-2}$ provided that

(*i*) $(\alpha+1)\alpha(\alpha+1-\rho_2 U)(\alpha+2-\rho_2 U)c_1-2\lambda_1 U\alpha^2(\alpha+1-\rho_2 U)c_0=0$

or $(\alpha+1)(\alpha+2-\rho_2 U)c_1-2\lambda_1 U\alpha c_0=0$, if $\alpha+1\neq\rho_2 u$

(*ii*) $(\alpha+2)(\alpha+1)(\alpha+2-\rho_2 U)(\alpha+3-\rho_2 U)c_2-2\lambda_1 U(\alpha+1)^2(\alpha+2-\rho_2 U)c_1+\{f_1\alpha(\alpha-1)+f_2\alpha+f_3\}c_0=0$

(*iii*) $(\alpha+3)(\alpha+2)(\alpha+3-\rho_2 U)(\alpha+4-\rho_2 U)c_3-2\lambda_1 U(\alpha+2)^2(\alpha+3-\rho_2 U)c_2+\{f_1(\alpha+1)\alpha+f_2(\alpha+1)+f_3\}c_1+2k\lambda_1 U(\alpha+1)c_0=0$

(*iv*) $(\alpha+n+2)(\alpha+n+1)(\alpha+n+2-\rho_2 U)(\alpha+n+3-\rho_2 U)c_{n+2}-2\lambda_1 U(\alpha+n+1)^2(\alpha+n+2-\rho_2 U)c_{n+1}+\{f_1(\alpha+n)(\alpha+n-1)+f_2(\alpha+n)+f_3\}c_n+2k\lambda_1 U(\alpha+n)c_{n-1}+k^2c_{n-2}=0$, for $n\geq 2$.

Assuming that $\frac{c_{n+1}}{c_n}\to l$ as $n\to\infty$, we have $l=0$ from the above expression. This shows that the series thus obtained will be absolutely and uniformly convergent for all values of x_1.

Now our indical equation is $\alpha(\alpha-1)(\alpha-\rho_2 U)(\alpha+1-\rho_2 U)=0$.

which gives $\alpha=1, 0\ \rho_2 U \& \rho_2 U-1$.

Case (*i*). If $\rho_2 U$ is not an integer, the four solutions are

$$V_1=\left[W\right]_{\alpha=1}, \quad V_2=\left[\frac{\partial W}{\partial \alpha}\right]_{\alpha=0}, \quad V_3=\left[W\right]_{\alpha=\rho_2 U}$$

and

$$V_4=\left[\frac{\partial W}{\partial \alpha}\right]_{\alpha=\rho_2 U-1}$$

Case (*ii*). If $\rho_2 U=0, 1$, or any other integer, the solutions may be modified according to the method of Frobenius.

Now we have to find the Particular Integral of (12).

Here
$$\Delta=\begin{vmatrix} V_1''' & V_2''' & V_3''' & V_4''' \\ V_1'' & V_2'' & V_3'' & V_4'' \\ V_1' & V_2' & V_3' & V_4' \\ V_1 & V_2 & V_3 & V_4 \end{vmatrix}$$

$$2\int^{\lambda_1 U x_1+(\rho_2 U-3)} \frac{}{x_1} dx_1$$

and its value is $ce=cx_1^2(\rho_2 U-3)\, e^{2\lambda_1 U\lambda_1}$, ..$c$ being a constant.

Let Δ_r be the minor of V_r''' for $r=1, 2, 3$ & 4. Then the Particular Integral[2] is given by

$$\sum_{r=1}^{4} V_r \int \frac{R_{x_1}\Delta_r}{x_1^2\Delta}\, dx_1$$

The expression within the Integral is of the form

$\int x_1^{l_1} e^{\gamma x_1}\, dx_1$ and this can be solved.

Thus we get the solution of (12) to be

$$V=\sum_{r=1}^{4} V_r\left\{\bar{c}_r+\int \frac{R_{x_1}\Delta_r}{x_1^2\Delta}\, dx_1\right\}$$

Hence a complete solution of the problem under consideration can be found

My grateful thanks are due to Prof A C Banerji under whom I have worked out this problem

References

(1) Lamb *Hydrodynamics* 6th Edn 1932 § 34
(2) Loc cit § 191
(3) Forsyth *A Treatise on Differential Equations* 4th Edn 1914 § 75

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1949

PART I] SECTION A [VOL. 18

CONTENTS

PAGE

Humus and Coal as Manures

By N. R Dhar 1

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) ; Rs. 5/8 (Foreign)

67489

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1949

PART II] SECTION A [VOL. 18

CONTENTS

PAGE

Determinations of Elastic Constants of Gels by Ultrasonic Method

By Arvind Mohan Srivastava 51

Action of Light on Colouring Matters and their Oxidation

By N R Dhar 65

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1949

PARTS III] SECTION A [VOL. 18

CONTENTS

PAGE

On the Flow of Air Through Chink of a Reed Vibrator
By Ram Gopal Chatterji 89

A Qualitative Study of Flame Test for Tin, Gold and Bismuth
By R. C. Mehrotra 103

The Nature of Hydrated Copper Hydroxide Precipitated and Aged Under Different Conditions
By R. C. Mehrotra and S. Ghosh 111

Physico-Chemical Studies in the Formation of Complex-Stannioxalates
By Arun K. Dey and A. K. Bhattacharya 121

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1949

PART IV] SECTION A [VOL. 18

CONT NTS

PAGE

"Note on the Harmonic Polars and the Cayleyan of a cubic"

By Haridas Bagchi 125

Studies in the Optical Rotation of Abietic Acid

By S P Mitra 137

ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India): Rs. 5/8 (Foreign)

PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES INDIA

1949

PARTS V & VI] SECTION A [VOL. 18

CONTENTS

	PAGE
Absorption Measurements at low Frequencies in some Liquids *By Gurudeva Sharan Verma*	149
Theory of the Clarionet *By R. N. Ghosh*	159
A Note on the Principal Radii of Curvature *By P. B. Bhattacharya*	167

ALLAHABAD

PUBLISHED BY THE COUNCIL

Rs. 5 (India): 5/8 (Foreign)

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART I] SECTION A [VOL 18

HUMUS AND COAL AS MANURES

By

N R DHAR

Manuring with Nitrogen Rich Compounds and Loss of Nitrogen

From ancient times animal matter like blood fish bone meal, tankage, wool residues, meat residues guano human excreta etc has been used as manure, but the mechanism of their action has been cleared up only in recent years The carbon nitrogen ratio of these substances is less than 10 and when they are mixed with soil, the carbonaceous compounds and the proteins are oxidized with the liberation of carbondioxide and ammonia which in its turn is further oxidised to nitrite and nitrate which is the chief plant food material The above mentioned substances are known to be fairly quick acting manures in crop production Researches carried on in the Allahabad University have established that when nitrogenous fertilizers are added to the soil, a good deal is wasted as nitrogen gas without benefit to the crop or soil When 100 lbs of ammonium sulphate are added per acre of land under cultivation about 40 lbs are available to the crop, but 60 lbs are wasted as nitrogen gas under ordinary conditions of cultivation In our recent experiments the following results have been obtained with different nitrogenous substances .—

Substances mixed with soil	Period of exposure	Loss of nitrogen %		Percentage loss of of nitrogen in unit time (per month)	
		Light	Dark	Light	Dark
(1) Ammonium Sulphate	2 month	55 [illegible]	43 2	27 8	21 [illegible]
(2) Ammonium Phosphate		67 5	58 4	33 8	29 2
(3) Ammonium Nitrate		28 9	21 0	14 5	10 5
(4) Ammonium Tartrate		47 6	38 3	23 8	19 2
(5) Ammonium Oxalate	,,	56 6	28 6	18 3	14 3
(6) Ammonium Citrate	4½ months	69 3	54 8	22 1	12 2
(7) Urea	5½ months	17 4	35 1	10 5	7 8
(8) Hippuric Acid	4½ ,,	42 3	23 2	9 4	5 2
(9) Gelatine	4½	40 1	23 2	8 9	5 2
(10) Oil-Cake	5½ ,,	35 9	29 0	6 5	5 3
(11) Blood	6 ,,	54 1	48 7	9 0	8 1

The amount of nitrogen initially present in the above nitrogenous compounds varied from about 0 25 gram to 0 5 gram in 100 grams of soil. Moreover, with such manures acidity is produced. With ammonium nitrate better result is expected and obtained because half of the nitrogen is in the form of nitrate and hence the

loss is less than with ammonium sulphate. With ammonium nitrate no acidic residue is added to the soil permanently as the nitrate ion is either absorbed by the plant or leached away in the under ground soil. With sodium or potassium nitrate certainly better results are expected but when the carbonaceous substance in the soil is large , there is always the possibility of the formation of nitrite and perhaps ammonium salt and thus loss of nitrogen as nitrous acid and nitrogen gas specially in acid soils and there is considerable leaching with nitrates. Hence these inorganic fertilizers although they are quick-acting and readily available in our industrial civilisation, do not enrich the soil permanently as there is hardly any addition of humus with such fertilizers. The great advantage with such fertilizers is that they can be added to the growing crop or as a top-dressing material and no time interval is needed between the addition of the fertilizer and the sowing of the crop. The disadvantages are (1) much loss of nitrogen in the gaseous state specially with ammonium compounds (2) the production of acidity (3) leaching (4) no humus addition (5) and specially in our soil which is on the alkaline side, there is the possibility of a loss as ammonia gas.

Fixation of Atmospheric Nitrogen in Soil and Formation of Humus

For over twenty-five years we have been utilising different energy producing materials in enriching the soil from the nitrogen point of view. We have tried all the sugars and observed that when they are mixed with soil, they are oxidised finally into carbondioxide and water with the liberation of energy which is utilised in fixing the nitrogen of the air on the soil surface. If the system is illuminated by sunlight or artificial light, the light is absorbed by the system and the nitrogen fixation is greatly increased. This utilisation of light in enriching the soil takes place under natural conditions all over the world and appears to be next in importance to photosynthesis in plants. We have utilised all sugars, starch, glycerol, filterpaper, lignin, butter, melted and clarified butter known as *Ghee*

in India, and found that all these materials though free from nitrogen undergo oxidation in soil in presence and absence of sunlight. In all these cases the nitrogen addition to the soil takes place without the addition of nitrogenous manures. We have also observed that molasses, press mud, plant-residues, leaves, farm-yard manure, cow-dung, straw, saw-dust etc. with carbon/nitrogen ratio varying from 100 to 15 not only add the nitrogen they contain but fix atmospheric nitrogen as well. The fixation of nitrogen is greater, the greater the carbon/nitrogen ratio of the energy material. In this process also sunlight or artificial light is utilised in increasing the nitrogen status. Marked fixation also takes place under sterile conditions.

It is interesting to note that greater nitrogen fixation is observed with wheat straw than Neem leaf (Malia Azadiractta Lina). Cowdung comes third in order, the efficiency of nitrogen fixation (amount of nitrogen fixed per gram of carbon oxidized) being 24.8 with wheat straw, 21.5 with Neem leaf, 20.3 with cowdung in sunlight. In the dark the efficiency is less than half. This behaviour can be explained from the difference in their carbon-nitrogen ratio.

The carbon-nitrogen ratio of the materials are recorded below :—

Substances	Total Carbon%	Total Nitrogen%		C/N ratio
(1) Cowdung	8.06	0.414		19.44
	9.37	0.422		22.20
	6.52	0.362		18.00
			Mean	19.88
(2) Neem leaf. (Melia Azadiractta Lina).	21.31	0.670		31.8
	18.57	0.654		28.4
	17.98	0.642		28.0
			Mean	29.4
(3) Wheat straw	38.06	0.5742		66.3
	38.06	0.5707		66.6
			Mean	66.45

It is clear that the greater the carbon-nitrogen ratio of the material, the greater is the efficiency of fixation of nitrogen.

On the application of farmyard manure in Rothamsted for a number of years the soil nitrogen which was originally 0.122% rose to 0.236% from 1842 to 1914. Repeated additions of ammonium sulphate or sodium nitrate did not improve the nitrogen status of soils at all. Similar results as recorded below were obtained by us at Allahabad. Moreover there is more nitrogen in the soil covered with grass than when there is no grass cover :

Soils	Total C%	Total N%	NH_3–N%	NO_3 N %
(1) Not covered with grass.	0.386	0.0388	0.0024	0.0012
(2) Covered with grass for 6 months	0.633 0.658	0.0630 0.0656	0.0039 0.0039	0.0021 0.0029
(3) Covered with grass for the whole year.	0.790	0.0786	0.0051	0.0025

It is interesting to note that the percentage of nitrogen in the fields rose from 0.0386 to 0.094 after the first application of cowdung and to 0.1517% on the second addition and to 0.2000% after the third application of cowdung. The corresponding results with Neem leaf are as follows : –

Original nitrogen content	0.0386%
After first application	0.0628%
After second application	0.0815%
After third applicatipn	0.1021%

The foregoing results show conclusively that repeated application of cowdung and neem leaf enrich the soil markedly by increasing its nitrogen content and humus by fixation of nitrogen and retaining the added nitrogen as well, i.e., the nitrogen of the materials added.

It is estimated that 35 billion kilograms, i.e., 34750 million tons of cellulose containing 13750 million tons of carbon are added every year to the earth. From our experiments we find that 40 % of the

carbon is oxidised in our climatic conditions in four or five months and even if the same amount be taken to be oxidised on the surface of the earth in the whole year, it would mean that 5500 million tons of carbon are oxidised every year. On a moderate estimate of 15 mgms. nitrogen fixation per gm. of carbon oxidised in sunlight about 82.5 million metric tons of nitrogen are added to the earth by fixation provided 40 % of the carbon added is oxidised. We can conclude that out of total 82.5 million tons at least 50%, i.e., 41.25 million tons of nitrogen are fixed in soils by absorption of solar light. The total output of nitrogen fixed synthetically in the factories of the world in 1937 was 3.54 million tons, i.e., 1/12th. of what is obtained by fixation under natural conditions by the utilization of sunlight.

It is interesting to note that although the velocity of oxidation of organic matter in sterile condition is smaller than in unsterile conditions, the efficiency of nitrogen fixation in sterile conditions is of the same order as that obtained in the unsterile experiments as is clear from the following data :—

Condition	Material used	Period of exposure (Months)	Carbon oxidized % during the whole period	Carbon oxidized % during one month	Amount nitrogen fixed in mgm. per 100 gms of soil	Efficiency in sunlight
Unsterile	Cowdung	4	0.475	0.119	9.8	20.7
Sterile	Cowdung	4	0.303	0.076	4.6	15.2
Unsterile	Neem leaf	4	0.402	0.101	9.1	22.6
Sterile	Neem leaf	4	0.221	0.055	2.8	17.2
Unsterile	Wheat straw	12	0.605	0.050	14.2	23.8
Sterile	Wheat straw	12	0.319	0.026	5.5	17.4

Influence of Light on Nitrogen Fixation by Azotobacter in Presence of Calcium Carbonate

In 1941 Dhar and Seshacharyulu (Proc. National Academy of Sciences, India 1941, **11**, 97) reported the fixation of 11.75 milligrams of nitrogen in light and 18.5 milligrams in the dark in 100 cc of mannitol in tap water containing 2 grams mannitol, 0.02 grm dipotassium hydrogen phosphate and 1 gram calcium carbonate containing a pure culture of Azotobacter after exposure for sixty-three days to sunlight and a comparative set covered with black cloth. At that time the carbon remaining unacted upon was not estimated and hence the efficiency, i.e., the amount of nitrogen fixed per gram of carbon oxidised could not be determined. Recently Dhar and Ghildyal have extended these experiments and have obtained the following results using the same medium after innoculating with an Azotobacter culture :—

After 6 month's exposure in April to September 1949. 500 cc containing the above materials and Azotobacter were used in these experiments

LIGHT	*DARK*
Carbon oxidised 1.3 gram.	Carbon oxidised - 1.4 gram.
Nitrogen fixed- 20.8 milligrams.	Nitrogen fixed 17.5 mgms.
Efficiency —16 milligrams. per gram of carbon oxidised.	Efficiency -12.5 mgms. per gram of carbon oxidised.

After 65 days' exposure in November, December 1949 and January 1950.

LIGHT	*DARK*
Carbon oxidised- 2.02 grams	Carbon oxidised 2.17 grams.
Nitrogen fixed —25 milligrams.	Nitrogen fixed—24 milligrams.

Efficiency per gram of carbon oxidised. —12.4 milligrams.	Efficiency per gram of carbon oxidised.—11milligrams.

After 110 days' exposure in November, December 1949 and January and February 1950.

LIGHT	*DARK*
Carbon oxidised—2.174 grams.	Carbon oxidised—2.011 grams.
Nitrogen fixed –19.75 mgms	Nitrogen fixed– 16 milligrams.
Efficiency - 9 mgms per gram of carbon oxidised.	Efficiency—7.9 mgms per gram of carbon oxidised.

In the last two sets of experiment, the carbon added as mannitol was 3.054 gms but the whole was not oxidised even in 110 days.

It is clear, therefore, that the efficiency of nitrogen fixation in presence of calcium carbonate with a culture of Azotobacter fed with mannitol is appreciably greater in light than in the dark due to the absorption of light by calcium carbonate although the carbon oxidized in two cases is slightly less in light than in the dark.

Humus in composts is less than in direct addition of plant materials to soil without composting.

The composts prepared according to the Indore method contain about 0.9 % nitrogen and about 13% carbon and potash, phosphate and other minerals. In other words, if one ton of such a compost is added per acre of land, we are adding approximately 18 lbs of nitrogen and about 220 lbs of carbon as humus and some potash, phosphate and other minerals. A part of the nitrogen of the compost is actually available to the crop. One ton of such compost per acre does not provide the adequate quantity of nitrogen for a good crop yield. On the other hand , if one ton of wheat straw containing 0.6 % nitrogen is added to the soil before composting it adds 13 lbs of nitrogen and 1000 lbs of carbon. A good deal of this carbon is oxidised in three or four months. This may lead to the fixa-

tion of about 20 lbs of additional nitrogen Hence, 1 ton of undecomposed wheat straw adds to the soil almost double the nitrogen and humus obtained with the composted material But in this case a time interval should be given between the addition of straw and the growing of a crop

In other words, a new method of manuring land with carbohydrates, celluloses, lignins or any energy material with a carbon/nitrogen ratio much greater than 10 has been developed So far materials with carbon nitrogen ratio greater than 10 were allowed to ferment and undergo oxidation as in composting, and when the carbohydrates and other energy materials were partially oxidised and the carbon/nitrogen ratio of the materials approached 10, the product was used as a compost in top-dressing in cultivation But we have been able to establish that all energy materials when added to the soil enrich it from the humus and nitrogen point of view and in this process the energy of oxidation as well as solar light is utilised for soil improvement, by fixing the nitrogen of air and this is the chief source of soil nitrogen all over the world

With substances like urea, blood, guano, gelatine, wool-residue etc , the carbon/nitrogen ratio being less than 10, favourable effect to crop production is observed when the crops are grown within two or three weeks after the addition of such manures With these manures also there is a marked loss of nitrogen in the gaseous state although there is the formation of a certain amount of humus depending on the carbon/nitrogen ratio of the manure The greater the carbon/nitrogen ratio of the starting materials the greater is the production of humus and greater is the residual effect

Oil-cake should be cheap in tropical countries and should prove to be a good manure as the carbon-nitrogen ratio of most oil-cakes is of the order 10 1, *i e*, the composition is practically the same as that of soil humus, but the difficulty of the oil-cake is that the oils present in such cakes are oxidised in the soil with great difficulty It seems that they form oleates, palmitates, stearates of calcium, iron, aluminium etc which are very sparingly soluble in water and are

not readily oxidised. Since the carbon/nitrogen ratio is practically that of soil humus and because the oil-cakes remove the alkalinity of our soils which are on the alkaline side as in the north of India, they should be extensively used in this country provided the price is not too high. They contain 5—7% nitrogen and can readily fix nitrogen when mixed with either molasses or plant leaf.

Humus Formation with Soluble Carbohydrates, Glycerol and Fats.

Molasses, press-cakes and other waste materials of sugar industry can fix nitrogen readily in our soils within a month or so. With alkali soils they are specially beneficial. Although there is no cellulose or lignin in such materials but there is appreciable humus formation and residual effect because of the formation of unstable compounds containing carbohydrates and proteins. The proteins are formed by nitrogen fixation either through the intervention of micro-organisms or from physico-chemical agencies. The generally accepted view is that humus consists chiefly of ligno-proteins but the humus obtained from molasses is a good source of nitrogen to crops and creates residual effect in soils, specially marked in paddy cultivation. In the animal body the whole of the carbohydrate ingested is not oxidised but a part is preserved as glycogen. It is worth while examining whether the glycogen is in combination with the body or food protein or not. We have frequently observed that when molasses is added to our soils neutral or alkaline either in fields or in dishes the C/N ratio which after the addition of molasses may be very high but it tends to become 10:1 in course of time showing the formation of humus in such soils. Similarly when glycerol or any other carbohydrate or fats are added, the carbon/nitrogen ratio converges to 10:1 in time, although, the quantities of carbon and nitrogen present are greater than those in the original soil. Hence humus formation is possible with carbohydrates, glycerol, fats etc. as with cellulosic materials, lignins, cotton-wool, filter-paper, leaves etc.

No Decrease in Available soil Nitrogen on Addition of Sugars, Starch and Glycerol to Tropical soil.

The most important point with soluble carbohydrates, glycerol and starch as manures in tropical soil is that the available nitrogen goes on increasing from the very beginning, the ammoniacal nitrogen goes on increasing steadily, the nitrate nitrogen never goes down, remains stationary for some time, but increases later on. This behaviour of soluble carbohydrate manuring in our country is in marked contrast to the existing literature in Europe and in Hawai where marked fall of nitric nitrogen has been observed on the addition of sugar to soil. With cellulosic or ligno-cellulosic materials and fats in tropics there is an initial fall of ammoniacal and nitric nitrogen. The manuring value of soluble carbohydrates is much quicker than with celluloses, lignins and fats, as will be evident from the following tables.:—

Plots 4 feet × 4 feet Containing 10 kgms molasses

LIGHT

Date	NH_3-N %	NO_3-N %	Total N%	Total carbon %	Azotobacter per gm of dry soil in millions.	Total Bacteria per gm of dry soil in millions.
13-2-1937. (Original soil)	0.0006	0.0014	0 0310	0.3472	0.9	12.0
9-3-1937	0.0012	0.0016	0 0344	1.7708	12.5	38.0
26-4-1937	0.0016	0.0016	0.0388	1.4136	75.0	245.0
12-7-1937	0.0028	0.0016	0.0456	0.6875	155.0	385.0
25-9-1937	0.0019	0.0017	0 0461	0.4728	115.0	305.0

Nitrogen fixed per gram of carbon oxidised—8.9 mgm

DARK

Date	NH_3-N %	NO_3 N %	Total N%	Total carbon %	Azotobacter per gm of dry soil in millions	Total Bacteria per gm of dry soil in millions.
13-2-1937 (Original soil)	0.0006	0.0012	0.0300	0.3240	1.0	13.0
9-3-1937	0.0010	0.0015	0.0328	1.7732	16.0	48.0
26-4-1937	0.0013	0.0015	0.0394	1.4702	120.0	365.0
12-7-1937	0.0014	0.0015	0.0375	0.7854	290.0	615.0
25-9-1937	0.0013	0.0016	0.0388	0.4468	315.0	645.0

Nitrogen fixed per gram of carbon oxidised—3.56 mgm.

1 Kilogram of soil plus 20 grams of filter paper

LIGHT

Date	NH_3-N %	NO_3-N %	Total N%	Total carbon%	Moisture %	Azotobacter per gm of dry soil in millions.
30-10-1936 (Original soil)	0.0011	0.0020	0.0540	0.567	2.2	2.4
22-12-1936.	0.0008	0.0018	0.0540	...	3.8	3.7
20-1-1937.	0.0007	0.0016	0.0560	...	3.1	7.7
20-3-1937.	0.0006	0.0014	0.0583	...	3.0	12.5

Date	NH_3N%	NO_3-N %	Total N%	Total carbon%	Moisture %	Azotobacter per gm of dry soil in millions.
7-5-1937.	0.0006	0.0012	0.0664	...	3.5	20.5
7-6-1937,	0.0006	0.0011	0.0677	...	3.1	27.2
8-7-1937.	0.0007	0.0014	0.0666	0.7012	...	18.0
13-9-1937.	0.0014	0.0021	0.0646	0.6704	...	12.0

Nitrogen fixed per gram of carbon oxidised—18.1 mgm(Calculated)

1 Kilogram of soil plus 20 gms filter paper.

DARK

Date	NH_3N%	NO_3-N %	Total N%	Total carbon%	Moisture %	Azotobacter per gm of dry soil in millions.
30-10-1936 (Original soil)	0.0011	0.0020	0.0540	0.5670	2.2	2.4
22-12-9136	0.0007	0.0015	0.0540		4.8	4.3
20-1-1937	0.0006	0.0012	0.0540		4.2	5.7
20-3-1937	0.0006	0.0010	0 0552		4.0	25.5
7-5-1937	0.0006	0.0009	0.0567		3.0	60.0
7-6-1937	0.0006	0.0009	0.0575			80.0
8-7-1937	0.0007	0.0009	0.0583			92.5
13-9-1937	0.0008	0.001	0.0608	0.6486		145.0

Nitrogen fixed per gm of carbon oxidised 9.2 mgm (Calculated)

1 Kilogram soil plus 20 gms butter

LIGHT

Date	NH_3N%	NO_3-N %	Total N%	Total carbon%	Moisture %	Azotobacter per gm of dry soil in millions.
13-10-1936 (Original soil)	0.0014	0.0032	0.0570	0.6156	1.8	5.1
14-11-1936	0.0015	0.0032	0.0570	1.4195	2 6	5.8
15-12-1936	0.0016	0.0032	0.0570	1.3883	3.1	7.6
13-1-1937	0.0014	0.0029	0.0570	1.3497	3.5	9.5
18-2-1937	0.0009	0.0024	0 0591	1.1968	3 0	12.0
11-5-1937	0.0007	0.0011	0 0617	0.9381	3.0	35.0
11-9-1937	0.0006	0.0010	0.0646	0.6659	3.0	25.0
12-10-1937	0.0009	0.0011	0 0626	0.6318	3.2	15.6

Nitrogen fixed per gram of carbon oxidised—10 07 mgms.

1 Kilogram soil plus 20 grams butter.

DARK

Date	NH_3-N %	NO_3-N %	Total N %	Total C %	Moisture %	Azotobacter per gram of dry soil in millions
13-10-1936 (Original soil)	0.0014	0.0032	0.0570	0.6156	1.8	5.1
14-11-1936	0.0014	0.0032	0 0570	1.4564	3.9	6.6

Date	NH_3-N %	NH_3-N %	Total N %	Total % Carbon	Moisture %	Azotobacter per gm of dry soil in millions.
15-12-1936	0.0015	0.0030	0.0570	1.4278	4.0	8 5
13-1-1937	0.0002	0.0028	0.0570	1 3962	4.4	14.6
18-2-1937	0.0007	0.0021	0.0583	1.2854	4.0	20.0
14-5-1937	0.0006	0.0010	0.0591	1.0952	4.0	50.0
11-9-1937	0.0006	0.0900	0.0600	0 7456	3.5	70.0
12-10-1937	0.0007	0.0009	0.0591	0.6036	3.8	58.8

Nitrogen fixed per gram of carbon oxidised—4.22 mgm.

Nitrogen Fixation and Humus Formation are Quicker and Greater in sandy soils than in clay soils

When sand is used as medium, the nitrogen fixation is much greater than with soil as the nitrogen content of sand is much smaller than that of soil. The following results have been obtained using sand as a medium :—

100 gms sand with different amuonts of energy materials.

Exposure 2½ months.

Substance		%C Initial	%N Initial	%C Final	%N Final	Efficiency i. e. nitrogen fixed in milligrams per gram of carbon oxidised
Butter	Light	1.2846	0.0101	1.0625	0.0164	28.3
,,	Dark	1.2846	0.0101	1.1543	0.0122	15.9
Lactic	Light	1.3113	0.0104	1.0066	0.0181	25.3
acid	Dark	1.3113	0.0104	1.1387	0.0130	14.8
Mustard	Light	1.3099	0.0148	1.0388	0.0221	26.5
oil	Dark	1.3099	0.0148	1.1634	0.0169	14.1

Exposure 5 months.

Butter	Light	1.2846	0 0101	0 8540	0.0228	27
,,	Dark	1.2846	0.0101	1.0355	0.0138	15
Lactic	Light	1.3113	0.0104	0.7211	0.0246	24.1
acid	Dark	1.3113	0.0104	0.9935	0.0149	14.1
Mustard	Light	1.3099	0.0148	0.8086	0.0274	25
oil	Dark	1.3099	0.0148	1.1114	0.0187	13

When soil is used instead of sand as medium with the above substances as energy materials the efficiency of nitrogen fixation both in light and dark becomes much less as is evident from the following results :—

100 grams soil mixed with different amounts of energy materials.

Exposure for 4 months

Substance		%C Initial	%N Initial	%C Final	%N Final	Efficiency
Butter	Light	1.3548	0.0410	1.0752	0 0445	12.3
,,	Dark	1.3548	0 0410	1.2072	0.0419	6.2
Lactic acid	Light	1.3734	0 0411	0.9912	0.0453	10.9
	Dark	1.3734	0 0411	1.1693	0.0423	5.9
Mustard oil	Light	1.3374	0.0408	1.0518	0.0443	12.2
	Dark	1.3374	0.0408	1.1786	0.0418	6.4

Exposure for 8 months

Butter	Light	1.3548	0 0410	0.8213	0.0474	12
,,	Dark	1.3548	0.0410	1 0810	0.0427	6.2
Lactic acid	Light	1.3734	0.0411	0.6709	0.0486	10.7
	Dark	1.3734	0.0411	0.9786	0.0434	5.8
Mustard oil	Light	1.3374	0.0408	0.7933	0.0473	11.9
	Dark	1 3374	0.0408	1.0034	0.0427	5.9

These results show that with sand which is more porous than soil the velocity of oxidation of organic matter both in light and dark is greater than in soil. Moreover, the total nitrogen content being smaller than in soil the efficiency of nitrogen fixation is greater in sand than in soil; a sandy soil can be more readily enriched from the nitrogen stand-point by the addition of organic matter than a clay soil, but the nitrogen fixed is lost more readily from sandy soils than from clay soils.

The foregoing experimental results show that when molasses which is readily soluble in water and rich in carbohydrates is added to the soil even after a month, the ammoniacal nitrogen, total nitrogen, Azotobacter numbers and total bacteria increase markedly both in light and in the dark. The nitrate nitrogen remains stationary at the beginning, then it increases. At no stage in the fixation of nitrogen on the addition of sugars, molasses, starch, glycerol etc., the sum of ammoniacal and nitric nitrogen, that is available nitrogen goes down in our soils although the total bacterial numbers go on increasing markedly. This behaviour is in marked contrast to the observations in temperate countries where sugars, when added to the soils, are known to reduce the nitric nitrogen content of soils. This is explained from the viewpoint that the sugars supply the energy requirement and cell materials for the multiplication of the bacteria, which absorb the available nitrogen from the soil for the formation of microbial proteins. It appears that in our soils the soluble carbohydrates are oxidized much more readily than in soils of temperate countries and in this process marked nitrogen fixation takes place both in light and in dark and the available nitrogen used up for the formation of microbial protein is more than compensated by the formation of available and total nitrogen due to the fixation of atmospheric nitrogen. The proteins formed in nitrogen fixation are also readily oxidized to available nitrogen in our soils. The available nitrogen and the sugars being readily soluble in water exist in the aqueous solutions and also partly adsorbed on the soil surface.

Decrease of available nitrogen with celluloses and fats although there is much of fixation.

On the other hand, although, there is nitrogen fixation by mixing lignin, celluloses and fats with soil as recorded above and the total nitrogen increases, there is no increase of ammoniacal or nitric nitrogen for a long time. It appears that the available soil nitrogen in these cases is partially taken up by the increased number of micro

organisms for their microbial protein. The velocity of the oxidation of cellulose, lignin and fats in the soil is much smaller than with soluble carbohydrates and hence the fixation of nitrogen and the formation of protein and available nitrogen with fats, lignins and celluloses are much smaller in an unit time than with soluble carbohydrates. Moreover, a part of the available nitrogen may also remain adsorbed not only on the soil surface but also on the unoxidised fat or cellulose or lignin which are insoluble in water. Hence in this latter case there is fall of available nitrogen, although there is increase of total nitrogen.

The foregoing observations are strongly supported by the recent experiments of S. Mattson and E. Koutler-Andersson (Ann. Agr. Col. Sweden **11**, 107-134, 1943) and E. Bennett (Soil Science 1949. **68**, 399) who have reported that ammonium hydroxide is strongly adsorbed by lignin and other organic substances when they are mixed with ammonium hydroxide and a current of oxygen is passed at 25° for 150 hours. The solution or suspension of lignin during the treatment became very dark. When complete methylation had preceded oxidation, lignin was insoluble and there was no change of colour. The ammoniacal nitrogen was 33% of the total nitrogen adsorbed. These workers have shown that a part of nitrogen adsorbed was resistant to the action of 72% sulphuric acid and strong alkaline solutions. A relatively high percentage of nitrogen added during oxidation remains bound even after drastic methylation. These results throw considerable light on the marked stability of the nitrogen compounds present in coals which are formed from cellulosic and lignin matter present in plant materials.

Nitrogen Fixation, humus Formation and residual effect of a manure.

A few years ago, in an article in "Nature" (Vol. 151, 338, 1943) I stated that the residual effect of a manure will depend on its power to fix atmospheric nitrogen. Such materials show residual or beneficial effect to a succeeding crop. This view point will be clear from the following considerations:—

When ammonium salts or nitrates are added to the soil, a better crop yield is obtained, but these materials hardly add any humus which requires both carbon and nitrogen. In such a case hardly any nitrogen is saved for the next crop. On the other hand, when urea, blood, rotten fish, wool residue, guano etc., which are nitrogen rich materials with a ratio of carbon/nitrogen less than 10, are added to the soil, fairly rapid nitrate formation takes place and the crop sown after a month or so, is benefitted. Due to the presence of a certain amount carbon in the compound an appreciable amonnt of humus, rich in fats, proteins and microbial cells, may be stored in the soil and a small residual effect may be observed in the succeeding crop, provided the time interval between the sowing of the crop and the addition of the manure is not large. If the time interval is large, the humus may be oxidised and the whole of the nitrogen may be lost. Similarly, leguminous green manures with a carbon/nitrogen ratio of 10 to 13 actually add a large amount of nitrogen to the soil, and if the acidity is not large, with a time interval of two or three months, a better crop may be produced.

But the residual effect in this case is not likely to last long. As a matter of fact, no practical farmer has reported any residual effect with substances like blood, urea, nor even in the case of composts. The Rothamsted results with green manure like clover show that the residual effect lasts for 3 to 4 years at most. On the other hand, with farmyard manure with a carbon/nitrogen ratio of 20 or more, the residual effect is more permanent.

In all our experiments with materials like molasses with a carbon/nitrogen ratio of about 40 or more, cow-dung (C/N ratio 20), neem leaf (C/N ratio 25), wheat straw (C/N ratio 65) etc.. we have always obtained marked fixation of nitrogen and humus formation both in light and in dark. Since with these materials added to the soil not only the humus corresponding to the originally present nitrogen, but also an additional amount corresponding to the fixed nitrogen is added, it is clear that with these materials the total nitrogen and humus added to the soil always exceeds the nitrogen and humus

actually added in the manure. Specially in cold countries where the oxidation processes are slow and the carbon/nitrogen ratio of the starting materials is high, the fall of the carbon/nitrogen ratio in one year may not be much and the carbon/nitrogen ratio may not reach the value 10 to 1. Hence the fixation of nitrogen and formation of humus may continue even in the second or third year after the addition of carbonaceous compounds. Since the carbonaceous compounds act as a marked protein sparer in soil as in the animal body, the processes of ammonification, nitrification etc., of the protein matter are slowed down and losses of nitrogen will be reduced to a minimum due to the presence of the carbonaceous compounds. Therefore, in these cases subsequent crops will be benefitted even without the addition of any manure as is observed in the classical Rothamsted experiments and elsewhere.

In composting, the aim is to save the nitrogen present in the material and to add it to the soil with approximately ten times its weight of carbon along with minerals and microorganisms, that is, in the form of humus. But in most experiments with composting, there is loss of nitrogen in addition to its being tedious and troublesome, as observed by workers all over the world.

The only difficulty in the direct addition of plant materials is that a time interval is needed between the addition of the carbonaceous substances and the sowing of the crop. But with molasses at the rate of 10 tons per acre, a time interval of 5-6 weeks is quite adequate in our country. With cow-dung six weeks is adequate and with Neem leaf 6-7 weeks. But straw requires 10-12 weeks. In cold countries the period may be about double of that in tropical regions. If our aim is to draw one crop every year, the addition of carbonaceous substances like farmyard manure or green plant residues at the rate of 8-10 tons per acre should work with a time interval of about six months and should produce beneficial results even in temperate climates. If the time interval has to be minimised, a few pounds of urea, blood or inorganic nitrogenous manures per acre (say 20—25 lbs per acre) should prove effective.

It is interesting to note that stubble and roots that are left in the fields after harvesting supply the following amounts of carbon to the soil per acre in pounds :—

Oats (1877), wheat (1914), rye (1730), barley (2186), red clover (3833) and lucerne (4610).

It has been reported in the dry farming sections of Nebraska by Russel in 1929 that an increase in available nitrogen effected by a legume may increase crop growth but may cause the reduction of soil moisture. This accounts for the tendency of crops to "fire" when following alfalfa. On the other hand, the addition of cellulose rich materials may cause a deficiency of available nitrogen. A solution of the problems consists in supplementing the use of nonleguminous materials with suitable nitrogenous fertilizers.

Humus liberates nitrate more slowly than ammonium salts

Since 1920 we have shown that a substance which is capable of taking up oxygen can readily retard the oxidation of another substance when mixed with it. This is a perfectly general phenomenon and is applicable to reactions *in vitro*, in the animal body, in the plant as well as in the soil. More than fifty years ago physiologists observed the marked protein sparing capacity of carbohydrates in the animal body. In a number of papers we have shown that organic substances like molasses, sugars, cellulose containing materials like leaves, plant residues, fats etc. markedly retard the velocity of oxidation of proteins, urea, amino acids, ammonium salts etc., when added to the soil. In the rapid oxidation of nitrogenous compounds there is marked loss of nitrogen in the gaseous state due to the formation and decomposition of the unstable substance, ammonium nitrite, which is an intermediate product in the processes of ammonification and nitrification of nitrogenous compounds. Hence nitrogenous compounds when mixed with carbonaceous compounds, as in humus undergo slower oxidation and liberate ammonia and nitrate for a longer period for the benefit of the crop than in the absence of carbonaceous materials. Moreover, in the slow liberation of nitrates, the danger of leaching is less. The

foregoing considerations clearly explain why ammonium salts or nitrates do not improve the nitrogen status of soils but organic manures can do so and that the nitrogen content can increase permanently only when the nitrogenous compounds are associated with carbon compounds.

From times immemorial, people have used organic compounds farmyard manure, leaves, vegetable residues in manure heaps because of their nitrogen contents. We were the first to emphasise that the greater the carbon /nitrogen ratio of such manures the greater is the nitrogen fixation and humus formation when mixed with soil.

Humus in which the carbon/nitrogen ratio is 10 or more can liberate ammonia and nitrate for a longer period and more slowly than the same amount of nitrogenous compound added to soil without carbonaceous compounds.

Even to-day, crop production is caused chiefly by the nitrogen of the humus present in all soils, as only 3 % of the world crop production has been attributed to artificial manures. In soils of cold countries the humus nitrogen is usually 2500—3000 lbs. per acre in the first 9″ of the soil and out of this 1—2%, *i.e.*, 25—50 lbs is in the form of ammonium salts and nitrates, *i e.*, available nitrogen If to this soil 20 lbs. of nitrogen in the form of ammonium sulphate or nitrate are added, beneficial effect to the crop growth is expected. On the other hand, in tropical countries the total nitrogen content in the soil is of the order of 1000—1200 lbs. per acre in the first 9″. But usually the available nitrogen is 10 % or more in such soils. Hence the available nitrogen in tropical soils is nearly 100 lbs. per acre. It appears that the addition of 20 lbs. of nitrogen from artificial, cannot be as effective as in temperate climates where the available nitrogen already present in the soil is less. The aim of scientific and constructive agriculture specially in tropics should be to increase the humus capital which readily gives out available nitrogen and minerals required for crop growth slowly without less danger of leaching than with artificial manures.

In forest soils all over the world the humus is greater than in arable mineral soils. But the liberation of ammonia and its oxidation to nitrate is controlled by (*a*) pH of the soil (*b*) the temperature and (*c*) the solar light. In acid forest soils the carbon/nitrogen ratio is much greater than 10 and hence the total nitrogen content and it availability is usually not high.

Acid soils have larger and alkali soils smaller carbon/nitrogen ratios than normal soils

The carbon/nitrogen ratio in certain forms of humus has been a puzzling phenomenon. From a study of data obtained by various workers, the conclusion was reached that the carbon/nitrogen ratio tends to become narrower as the age of the humus increases.

Studies by previous workers on the influence of soil treatment upon the ratio of humus decomposition, as measured by carbondioxide evolution show that the carbon oxidation slows down as the pH is more on the acidic side. This was also shown by Dhar and Pant in "Nature" (1942, **149**, 84).

When humus has a wide carbon/nitrogen ratio, as in the case in soils shortly after receiving large applications of plant materials or little decomposed manure or in the 'F' layer of raw humus forest soils, there is still considerably greater liberation of carbon as carbondioxide than of nitrogen as ammonia, with the result that the carbon/nitrogen ratio of the humus tends to become narrower. When the initial ratio was 17.9—1, no nitrate was produced in a sand culture. However, when the carbon/nitrogen ratio of the humus was 13.1—1, considerable nitrate was formed.

Work on mull soils has indicated that acids decrease the carbon oxidation and ammonia oxidation markedly. We have been reporting for a number of years that the greater the average temperature of the soil, the greater is the pH of the soil. This is certainly due to the fact that organic matter of the plant residues added to the soil in tropical countries is quickly oxidised leaving small amounts of humus and chiefly minerals in the soil. Thus, the pH of soils in Egypt and India

is greater than in soils of cold countries. This is a sort of auto-catalytic effect, as alkalis help oxidation of carbohydrates readily. On the other hand, in acid soils as in cold countries, for increasing oxidation, lime or calcium carbonate has been recommended.

In composting in Indore it has been found that the pH increases as the composting progresses and when the composting finishes, the pH is of the order of 7.3—7.4. It is interesting to note that as the pH goes to the alkaline side the total nitrogen in humus also increases.

Percentage of nitrogen in humus of tropical soils is greater than in temperate climates

This raises a very important issue. Although the total nitrogen in tropical soils is low, the percentage of nitrogen is higher than in humus of cold countries which are on the acidic side. It is clear, therefore, that manuring by carbohydrates and cellulosic materials for increasing the nitrogen status of a soil is certainly more profitable in tropical or semi-tropical countries than in cold countries, not only because the velocity of oxidation of carbohydrate materials is slower in cold countries and hence the nitrogen fixation is less pronounced, but the nitrogen fixed will be converted into ammonia and may not be available to the crop because of the lack of nitrate formation. In cold countries it has been repeatedly observed that the improvement of the nitrogen status of a soil depends on the calcium status as has been markedly emphasized by Hudig in Holland.

If a large dose of lime or calcium carbonate is added, the excess reacts with the ammonium salts and proteins with loss of nitrogen. S. K. Mukerji and N. R. Dhar observed that when large quantities of calcium carbonate are mixed with molasses and soil, the efficiency of nitrogen fixation is less than in presence of small doses of calcium carbonate. E. V. Seshacharyulu and N. R. Dhar found that the efficiency of nitrogen fixation with 2% carbohydrate and soil in presence of calcium carbonate is less than in its absence. Similarly M. C. Pant, H. L. Nigam and N. R. Dhar showed that in the study

of the loss of nitrogen in the nitrification of ammonium salts, the smell of ammonia is obtained when 1 or 2 gms. of calcium carbonate are added to 100 c.c. of ammonium salt solution and the loss of nitrogen is less with 1 gm of calcium carbonate. It is clear, therefore, that although calcium carbonate and other salts help in the coagulation of impervious soils, an overdose produces loss of fertility due to the loss of ammonia and nitrogen in the gaseous state.

S. C. Sen under my direction has worked with a very large number of soils collected from different parts of Bihar. His results show that when the pH values of alkaline soils varies from 9.2 to 8.6, the carbon/nitrogen ratio may have the low values 2.86, 3.41, 3.38, 4.15 etc. Sen has shown that soils collected from Ranchi (Bihar), which is 3000 ft. above sea-level, have pH values ranging from 4.4 to 5.2 and the carbon/nitrogen ratio varies from 11.4 to 20.3. A soil sample from Coonoor (Southern India) which is above 6000 ft. showed a pH value of 4.8 and carbon/nitrogen ratio of 11.6, the total carbon being 1.72% and nitrogen 0.148%.

In a recent article (Dhar and Pant : "Nature" 1942, **149**, 48) it was concluded from the experimental results obtained with soils of different countries that acid soils have higher carbon/nitrogen ratio and alkali soils smaller carbon/nitrogen ratios than surface neutral soils.

This conclusion regarding acid soils has been supported by recent work. Evans and Rost obtained the following results with Minnesota soils :—

(1) Chernozems	; pH—6.3 ; C/N—11.4
(2) Black prairie soils	; pH—5.4 ; C/N—11.8
(3) Podsols of North Central Regions	; pH—5.4 ; C/N—11.8
(4) Podsols of North Eastern Regions	; pH—4.6 ; C/N—15.1

Moreover, Nair (M. Sc. degree thesis, Travancore University 1945) working with black 'Kari' soils of Travancore occurring in

coastal plains alongside some of the back waters and adjoining the Arabain sea obtained the following results :—

pH—6.7 ; C/N—11.1
pH—5.1 ; C/N—16.2
pH —4.5 ; C/N —26.2
pH —4.7 ; C/N—27.2
pH —3.9 ; C/N—30.1

Hence, the higher the acidity of the soil, the greater the carbon nitrogen ratio, i.e., the smaller the nitrogen content of the soil.

Peat, lignite and other varieties of coal containing humus as manures.

As peat, lignite and other varieties of coal are believed to be formed chiefly from plant materials which have been used by us for manuring fields, the former materials should serve as manures also.

The typical analysis of humic acids prepared from humic coal is carbon 60.5%, hydrogen 3.34%, nitrogen 2.03%, sulphur 1.44% and ash 1.96%. The nitrogen content of humic acid is due to the presence of protein associated with them. Some of the nitrogen in the humic acid molecule is considered to be bound cyclically, the nitrogen having replaced a heterocyclic oxygen atom.

By the extraction of soil humus, humic acid preparations and peat, substances have been obtained which prove quite definitely the protein nature of nitrogen in the younger fossils.

C. A. Weber defined peat as follows :—

"Peat is an organic mineral formed out of dead cellulose-rich plants by special process of decomposition. It is soft in its natural moist condition and is very rich in water. Peat contains largely the elements, carbon, hydrogen, oxygen and in addition varying amounts of nitrogen, sulphur and ash".

Humus in peat, lignite and coals.

All the peats are rich in lignin-like complexes. It is generally assumed that nearly all the nitrogen in peat is in an organic form and

is not readily acted upon by micro-organisms in the undrained peat but is acted upon very slowly when conditions are made aerobic as by draining.

In addition to cellulose and pentosans various peats contain also hemi-cellulose and hence mannose, galactose, levulose and other pentoses are formed on hydrolysis of peat with dilute hydrochloric acid. The carbohydrates present in peat when mixed with soil and allowed to oxidize partialy cause nitrogen fixation.

During the formation of peat the woody matter becomes more or less disintegrated and the structure of the material both physical and chemical is greatly altered. This process is chiefly biochemical, the major part of the disintegration being brought about by the action of micro-organisms and fungi. The biochemical process may cease with only partial decomposition of the woody texture, leaving the peat in such condition that lignite or woody coals are formed later.

The second stage in the formation of coal is brought about by dynamo-chemical processes which greatly alter the physical and chemical properties of the hydrated peat formed during the biochemical decay. A further step is brought about by the application of intense pressure often resulting from an upward thrust of the earth's crust causing a further loss of water accompanied by liberation of carbon dioxide, carbon monoxide and other gases. The coal decreases in volume and is cemented together depending upon the temperature and pressure conditions thus yielding the different types of coals.

Nitrogenous compounds in coal

In the coalification process nitrogen originally present as amino or amido groups is converted to some other non-basic form which is not extracted by mineral acids. The nitrogen from younger fuels is removeable by mineral acids. It is believed that during coalification the reactive amino and imino groups which are present in the younger fuels are involved in reactions with other groups such as carboxyl, hydroxyl, carbonyl and methoxyl which convert the basic groups

into non basic groups, the nitrogen being held in a heterocyclic or else linearly linked between units of such complexity and negativity that the nitrogen loses its basic properties.

Evidence indicates that a large part of nitrogen in humic acid is also bound cyclically. From studies of solvent extraction, vacuum distilation, combustion, oxidation, hydrogenation, halogenation and hydrolysis of coals of various ranks, the nitrogen in coal can be pictured as being present mostly in a hetero-cyclic linkage.

It is well known that lignin is the material which resists oxidation much more than other carbohydrates. Even lignin when mixed with soil undergoes oxidation. Peat which is rich in lignin-like complexes fixes nitrogen and reclaims alkali soil. Similarly lignite and brown coal should be effective for both the purposes. Bituminous and anthracite coal should be less reactive. Very finely powdered coals of all types should be able to supply nitrates to the soil by slow oxidation of the hetero-cyclic and other nitrogenous compounds and also fix the nitrogen of air. This must occur much more so with peat, dopplerite and brown coal rather than with anthracite coal. In our recent experiments carried on with peat, brown coal (lignite) and bituminous coal in a finely divided condition mixed with soil, nitrogen fixation is observed more in light than in dark. We have also observed a marked beneficial effect of these materials on crop production with normal soils and in the reclamation of alkali soils.

It is believed that in composts about 8—10 % of the total nitrogen is in the available form and hence compost is a quick acting manure in comparison with coal, which is certainly more ancient and inert than the humus in most soils. But if the coal is very finely powdered and mixed well with the soil, it not only should impart its nitrogen to the soil gradually but should be able to fix atmospheric nitrogen in the process of its slow oxidation to carbon dioxide and this has actually been observed by us with bituminous coal and lignite. Coal is certainly cellulosic or lignin substances mixed with protein of animal

and plant sources with some decompositon products from fats, barks, waxes, resins but the reactive groups like carbonyl, carboxyl, hydroxyl, methoxyl and amino group seem to have been removed by the influx of time because chemical changes have taken place intramolecularly or by the interaction between proteins and the cellulose and the lignins. Although coal appears to be rather dead matter in comparison with compost or humus of soil but there is a redeeming feature in coal which is this : coal adds large quantities of carbonaceous substances which are less reactive than the carbonaceous substances present in plant residues. And hence on the addition of coal to a soil, the available soil nitrogen is not likely to be converted into microbial cells as happens when cellulose, lignin or fat is added to the soil. Microbial cells may not use all the available nitrogen in soils but some part of the available nitrogen may form chemical compounds or adsorption compounds with cellulose, fats or lignins and would not be available to the growing plants. Coal, dopplerite, peat or brown coal being more inert than fresh plant materials will not be reacted upon by microorganisms quickly but should definitely help aeration and perhaps increased water retention capacity of the soil. If one ton of coal containing 2% nitrogen and about 75 % carbon is added to the soil in a finely divided condition, the following results are obtained :—

(*a*) 44 lbs of total nitrogen will be added and this nitrogen may be available in 2 or 3 years ; (*b*) 1640 lbs of finely divided carbon will be added per acre and about 1200 lbs may be oxidised in about 2 or 3 years and this may lead to a fixation of about 30 lbs of nitrogen which will be utilised by crops. It appears, therefore, that coal should prove to be a moderately good nitrogenous manure specially to tropical soils when either added in a very fine state of division alone or mixed with molasses or cowdung or plant leaf, the younger varieties like peat, dopplerite, brown coal should yield better results than anthracite. There is no doubt that

coals are colloidal substances containing colloidal carbon peptized by large quantities of hydrocarbon like compounds consisting of partially deoxidised celluloses, lignins and small quantities of proteins. It seems that a part of proteins has passed into other stabler forms of nitrogenous substances.

As alkalis help oxidation, the oxidation of cellulose and lignin and coal when added to the soil will be more easy in tropical soils which have a tendency to be alkaline than in soils of temperate countries which are acidic. It is clear, therefore, that the foregoing considerations are more applicable to our soils than in cold countries where liming has to be taken recourse to if carbohydrate or coal manuring has to be adopted. With adequate amounts of lime or chalk and coal extremely well pulverised, moderately good results should be obtained specially with peat and lignite and bituminous coal which are abundantly present in European and cold countries. When mixed with calcium carbonate they should not only improve the calcium status but should also improve the nitrogen status of soils. When this mixture of peat and calcium carbonate or coal and calcium carbonate is very well mixed with soil by deep cultivation and aeration of soil which will be aided by the large surface introduced in the form of finely divided coal or peat, crop production should be improved.

The chief differences between composts or humus of the soil and coal are as follows :

(1 Coal is definitely more aged than compost.

(2) The carbon/nitrogen ratio of coals, even the younger ones, is greater than that in composts although acidic composts or humus or composts present under acid soil conditions have much larger carbon/nitrogen ratio than those prepared in neutral or alkaline conditions.

(3) The nitrogen present in coal is not chiefly in the protein condition as in composts.

(4) The number of micro-organisms in a definite weight is certainly larger in compost than in coal.

(5) The water retention capacity is less in anthracite and bituminous coal than in composts.

(6) The inertness of the organic ingredients in coal is greater than in composts.

These factors may be the chief reasons why coal is considered to be a stone and dead matter in comparison with plant residues, or humus present in the soil. Is there any other important criterion differentiating dead and living matter ? Is it possible to revive coal after mixing it with plant leaf, cowdung or sugar or agar or any surface-active substance ?

It is generally believed that the oxidisability of the products of photo-synthesis in the plant tissues decreases with the increase in the molecular weight or complexity of the molecules. The order seems to be as follows :—

Formaldehyde—glucose—canesugar—starch—cellulose—lignin. The case of protein synthesised in the plant kingdom is more complicated. Our experimental results show that amino acids like glycine, aspartic acid etc. are synthesised in the plant kingdom or *in vitro* by the action of nitrates on glycol, sugars, glycerol, organic acids etc. either by absorption of oxidation energy or solar energy or both aided by titania. These amino acids undergo polymerisation and condensation and form proteins.

In carbohydrate synthesis, starch is readily detected when plant leaf free from corbohydrate is exposed to light and that is why Sachs concluded that starch is the first product in photosynthesis. In our experiments in photo-oxidation of various carbohydrates, Palit and Dhar observed that the oxidation of starch is slightly greater than other soluble carbohydrates. In our recent experiments on the induced and photo-chemical oxidation of cellulose and lignin carried on by Dinesh Pant and Dhar, it is observed that both the substances

can be oxidised very slowly by air at the ordinary temperature. The oxidation of starch is very much greater than either that of cellulose or lignin. There is no doubt that in nature, both cellulose and lignin, are oxidised but much less readily than starch or sugars. It has been established in recent years that when plant materials are allowed to be oxidised in the soil, the soluble carbohydrates disappear first, then cellulose, finally lignin, which disappears with great dificulty. This is the position in aerobic condition where oxidation can take place with the help of micro-organisms and the presence of surface and light. In anaerobic condition it is believed that the same order of stability is also obeived but the speed of disappearance of organic substances is smaller and acids are produced in the first stage.

It is of interest to record here that in a recent paper Spoehr and Milner (Plant Physiology 1949, 24, 120) have described a method for determining the degree of reduction of the total organic matter of plant material from its elementary chemical composition. The degree of reduction is believed to be proportional to the heat of combustion and is an expression of the energy content of the material. With proteins condensation with lapse of time, goes on. The formation of skin, hide, hoof, horn etc. is a manifestation of polymerisation and condensation and these materials resist oxidation well. Similarly carbohydrate and celluloses and tanning materials can form barks of trees which also resist oxidation. It is clear, therefore, that when plant materials containing carbohydrates, pentosans, starch, cellulose, ligno-cellulose, lignin, bark, fats, resins, waxes, simple and complex proteins, are mixed with large amounts of soil, they undergo slow oxidation through the agencies of bacteria, fungi, chemical surfaces, catalysts, light etc. but the velocity of oxidation differs greatly depending on the nature of the material undergoing oxidation. The waxes, resins, barks etc. seem to resist oxidation more vigorously than even fats and lignins. Similarly the complex proteins also are stable. Moreover by the combination of some of the proteins and the lignin or cellulose or bark, humus like chemical compounds or adsorption compounds may be formed and these

not only supply ammonia and nitrate slowly but can give up potash, phosphate and other mineral matters slowly to the soil.

On the other hand, under anaerobic conditions, i.e., when coals are formed in nature the position may be as follows :—

Instead of carbon dioxide, as in the case of aerobic oxidation, methane, hydrogen, carbon monoxide are formed along with acidic substances. Frequently it has been observed that the acidity of the products of decomposition and oxidation is greater in anaerobic than in aerobic conditions. It is well known that the velocity of oxidation of carbohydrates decreases as the acidity of the system increases. Consequently the disappearance of plant materials is quicker in aerobic than in anaerobic conditions The acids produced in both aerobic and anaerobic conditions, more in latter than in former, act as preserver of the carbohydrate, lignin and cellulosic materials whilst they may help the decomposition and oxidation of protein substances to the ammonia stage and a part of the ammonia may be washed out. Hence it has always been observed that the carbon/nitrogen ratio of organic substances in soils is greater in acid media than in neutral or alkaline condition. In the virgin prairies and steppes rich in humus, the carbon/nitrogen ratio has generally been observed to be greater than 10 and these soils are acidic. After cultivation, the acidity falls off because of the oxidation of acidic substances and there is a fall in carbon/nitrogen ratio. Similarly the carbon/nitrogen ratio of the organic matter in peat, dopplerite, etc. is of the order of 30 or more and these materials are distinctly acidic. It is well known that most of the coals are also acidic and the carbon/nitrogen ratio of the coals may vary from 120 to 30 depending on the conditions of coalification. It is generally accepted that the carbon/nitrogen ratio of the wood from which coal is obtained is greater than that of the coal; in other words, the percentage of nitrogen in wood is smaller than that of coal.

In the Indore method of composting under aerobic conditions with carbon/nitrogen ratio of starting materials varying from 130

to 20 the compost formed has a carbon/nitrogen ratio ranging from 17 to 12 and pH 7.2 to 7.4. If such plant materials are composted in anaerobic conditions, the carbon/nitrogen ratio of the material formed is likely to be larger due to acidic conditions. In the Indore method of composting the temperature of the heaps may go upto 80°; this not only kills the micro-organisms and the weed seeds but also help in the liberation of carbon or charcoal or graphite like substances.

Carbon and nitrogen contents of coal

In coal formation water is believed to play as important a part as high temperature and pressure. Water freed from oxygen helps making the conditions in peat formation practically anaerobic and also help in the washing away of ammonia and other soluble compounds formed in the processes which consist of auto-oxidation and reduction, hydrolysis and decomposition, polymerisation etc., specially under high pressure. It is generally believed that plant, animal and micro-organic substances when covered with shallow water lead to peat formation which is the first step in coalification In this process dehydration and formation of black substances resembling charcoal or graphite in small quantities, takes place The material produced has a marked tendency to adsorb moisture because of its colloidal nature. Peat or dopplerite perhaps resembles the black material obtained by the action of strong sulphuric acid on cane sugar. This material swells and forms a jelly readily although it does not contain any nitrogen, it may be considered to be something like humic acid. If protein substances are present or added to it, unstable chemical compounds between protein and this jelly are likely to be formed as investigated by Page and co-workers (J. Agric Science, 1930, **20**, 460). It seems that in the coalification process the starting material may be peat or dopplerite, which chiefly consists of humic materials or the "fundamental jelly" as stated by coal specialists. This jelly like substance in course of time loses its activity and water retention capacity and chemical reactivity. Moreover, the protein matter originally present either as adsorption or chemical compound may be liberated due to the decrease of chemical affinity of the humic matter

and may undergo decomposition or hydrolysis or auto oxidation and reduction. In this process the carbon content increases and nitrogen status decreases chiefly due to the liberation of ammonia and its removal. This is supported by the fact that as the rank of the coal increases generally the carbon increases and nitrogen decreases, specially in anthracite coals which are the most ancient. This is clear from the following table which shows the relative composition on an ash-free and moisture-free basis :—

	Total carbon.	*Total nitrogen*
Wood	49–50 %	1.1 %
Peat	56–57 %	2.95 %
Lignite	72–79 %	0.98 %
Sub-bituminous	76 %	1.47 %
Bituminous	87 %	1.37 %
Semi-bituminous	89.1 %	1.40 %
Semi-Anthracite	92.1 %	1.20 %
Anthracite	94.4 %	0.71 %

Moreover , in coalification from peat or plant materials high temperature and pressure play a very important role and this helps in the carbonisation or formation of more charcoal or graphite like substances or perhaps the partial decomposition and stabilisation of the undecomposed nitrogenous substances. There is no doubt that the percentage of carbonaceous or graphite like matter is greatest in anthracite and least in peat or dopplerite, which is more allied to the initial plant or animal material or both than anthracite or bituminous coal.

In the high ranking coals the carbon chiefly exists as charcoal or graphite like substances and the nitrogen as nitrides, amides and in the hetero-cyclic condition and both the carbonaceous and nitrogenous substances can resist oxidation more markedly than those pre-

sent in peat or dopplerite. It is well known that plant residues, i.e. leaves, stems, roots, straw etc. not only add a part of the carbon and practically the whole of the nitrogen, they contain to the soil and can also manure the land by fixation of nitrogen by the partial oxidation of carbonaceous substances aided by light. Similarly the humus formed from plant residues either in the soil or compost heaps is certainly not as aged and as rich in charcoal or graphite like substances as anthracite coal. Consequently the humus which undergoes a slower oxidation in the soil than the original plant material is more readily oxidised when mixed with soil than anthracite or bituminous coal. It is clear, therefore, that the manurial value of the soil humus is quicker than that of anthracite or bituminous coal. It seems that the instability of a manure when mixed with soil and the speed of liberation of ammonia and nitrate will depend on the presence of chemical compounds resembling carbohydrates and celluloses, which are known to oxidise and liberate energy readily. On the other hand, when the manure is rich in charcoal or graphite like substances, which are more inert than carbohydrates, they are not likely to undergo ready oxidation in the soil.

Soot as a manure.

In this connection, it is interesting to note that soot obtained from domestic fires and industrial uses of coal is used by farmers as manure. The value depends partly on its physical effects on the soil and partly on its contents of nitrogenous and sulphur compounds. It is largely used as a top dressing for wheat in the early months of the year. The dead black colour of soot makes it a good absorbent of solar radiation so that the soil which has been treated with it is kept warmer than untreated land, whilst the nitrogenous compounds present in soot are valuable fertilizers. The carbon and nitrogen contents of coal and the soot obtained from it are as follows:—

	Carbon %	Nitrogen %
Soot	40.5	4.1
Coal	69.3	1.4

It has been reported that peat fires are kept burning all day and most of the night in the thatched houses and the only exit for the smoke is the doorway in the houses in the Hebrides. The thatch containing the soot is applied to the land for fertilization. The thatch is renewed annually. In the Hebrides, cows are housed under the same roof with the human beings and the cow manure is removed once a year and added directly to the land.

Molasses, soluble carbohydrates and glycerol when added to the soil are oxidised quickly and fix nitrogen and enrich the soil and can behave as quick acting, nitrogenous manures specially in tropical countries. On the other hand, when materials rich in cellulose, lignin and bark are added to the soil, the oxidation of the organic matter is much slower than in the previous case. Fats, resins, waxes also resemble the latter class. The case of mobil oil is peculiar. Although it is rich in carbon and hydrogen and is free from oxygen, it undergoes oxidation in the soil with very great difficulty and hence is not suitable as a quick acting nitrogen fixing material but these substances may increase the aeration and porosity of the soil. Saw-dust rich in lignin and lignino-cellulose behaves in the same way and markedly resists oxidation when mixed with soil. Charcoal or graphite when mixed with soil may increase the porosity and aeration but may not be able to fix nitrogen.

With protein substances, when mixed with soil, the simpler the constitution of the protein, the greater is its power to behave as a quick acting manure. Amino acids when added to the soil undergo ammonification and nitrification readily. Similarly human excreta containing amino acids and proteins, rotten fish etc. can behave as quick acting manures. Blood, oil-cake etc. containing fats do not undergo oxidation in the soils so readily and may not behave as very quick acting nitrogenous manure as the previous group. Hoofs, horns, hides etc. are formed as highly polymerised proteins of large molecular weight and when mixed with soil undergo very slow oxidation to ammonia and are not likely to act as quick acting manures. These complex protein matters are likely to remain in the soil for

long periods and may behave as slow reacting nitrogenous substances.

That the decomposition of pentosans decreases rapidly and the total carbon increases with the depth of peat indicate how quickly the original cellulose and other plant materials are transformed into humic products. Moreover the original woody structure is well preserved in some lignites and that is why the lignite or brown coal should be more valuabl as manure than anthracite coal.

Coal formation from plants.

It is clear from the existing literature that coal is formed under more anaerobic than aerobic conditions and coals are usually acidic. Consequently, the carbon nitrogen ratio of all samples of coal varies from 30 under the most favourable conditions to about 100 or more. The young varieties of coal like peat, dopplerite are acidic. Coals which are rich in sulphur should prove good manures for alkali soils.

In the process of coalification as in the sequence, wood (lignin and cellulose)→peat→brown coal (lignite)→bituminous coal→anthracite coal→graphite→diamond, there is not only dehydration or loss of water but there is also loss of oxygen over and above the loss of oxygen as water. In other words, auto-oxidation, and reductions involving the production of carbondioxide and perhaps carbon monoxide and organic acids take place along with the reduction of the cellulose or lignin or sugar. It is well known that glucose in presence of yeast undergoes the following change :—

$$C_6H_{12}O_6 = 2\ CO_2 + 2C_2H_5OH + 22\ K\ Cals$$

The alcohol is more reduced than sugar and the carbon dioxide is more oxidised than sugar. Hence this is a process of auto-oxidation and reduction The alcohol on dehydration may be converted into ethylene. Similarly the cellulose or lignin molecule in forming peat or coal must be partially converted into carbondioxide and perhaps carbon monoxide and organic acids and alcohols which on dehydration may yield hydrocarbons. The complex hydrocarbons may in turn break up into carbon and hydrogen.

Collodial carbon in humus and coal

The black material obtained in composting straw, plant residues, the black substance obtained in drains and in underground sewers and perhaps the black mass obtained by the action of concentrated sulphuric acid on sugars, filter paper, straw, saw-dust and the black, material in soil humus as well as that of coal, may be identical. Moreover, in composting thin layers of straw, though the temperature does not exceed 40° and there is a lack of high pressure, black masses are obtained. The mechanism of this blackening process is not very clear. In coal formation the temperature may go upto 100° or more and pressure may be high; but in peat formation which takes place under water, neither the pressure nor the temperature can be high. There is no doubt that cellulose, lignin and proteins take part in peat formation. As petroleum is also derived from vegetable and animal residues, it may be that hydrocarbons play a part both in coal and petroleum formation.

It seems that lignin can form woody coal but the cellulose, pectin and perhaps the sugars derived from pectin and cellulose may form jelly like substance or the 'fundamental jelly' of the coal scientists. This idea is supported by the fact that the black substance formed by the reaction of sulphuric acid on straw or cane sugar sets to a jelly readily. From the literature on the formation of coal, it is clear that apart from the mineral matter, carbohydrate, proteins, fats and waxes etc. of the vegetable world may form two important groups of compounds, one being the woody matter and the other, the jelly. The jelly may be the chief source of the volatile compounds in coal and the woody matter, the chief source of cokes, the protein, matter might have been incorporated in the jelly.

A part of the oxygen of the cellulose is lost as carbon dioxide and this is oxidation and the alcohol formed as the reduction product by partial dehydration can form a hydrocarbon. Hence the coal substance may be a mixture or a solid solution of colloidal carbon, a hydrocarbon and an alcohol. Consequently, the oxygen loss of cellulose or lignin may consist of two causes. Firstly, loss of carbon

dioxide and possibly carbon monoxide , and loss due to dehydration of alcohol forming a hydrocarbon which can break up into carbon and hydrogen gas. This explains the case with which, hydrocarbons, hydrogen, carbon monoxide etc. are given out on heating coal and its conversion into coke. Perhaps this mechanism of coalification throws light on the production of petrol in nature and also its production synthetically.

In our experiments with leaves, filter paper, saw-dust, cotton-wool, covered with water, both in light and darkness, even after one month, acids are obtained in aqueous solutions and there is appreciable blackening after three months, although the temperature never exceeded 40°. Cowdung is not acidic at all under these conditions.

With regard to the blackening under anaerobic conditions, a change takes place by which the organic matter is blackened, but the mechanism seems to be connected with some type of dehydration perhaps of the cellulosic material which forms the greater bulk of plant residues.

The decomposition of the bacteria, fungi, algae etc. which are present and active in the first stages of peat formation from vegetable and animal matter covered with water may produce black mass probably due to the liberation of carbon in the colloidal state. Similarly in composts and in the organic matters in drains, colloidal carbon may be formed by the partial decomposition of micro organisms.

Highly organised plants contain much less nitrogen than less organised plants. The nitrogen content of beach is 0.09 %, birch 0.10%, fir 0.05%, spruce 0.04%. On the other hand, bacteria contain up to 13 % nitrogen, algae 3.2 to 4.8, leaf moss 2.4 to 3.2 %, fern 1.6 to 2.4%, grass 1.6 to 2.4 % and swamp plants 1.6 %,

E. Terres (Proc. 3rd Intern conf. Bituminous coal, **2**, 797 (1931)) prepared artificial brown coals containing 4.16 % nitrogen by heating under pressure, peat moss containing 1.73% nitrogen after its

fermentation. The greater nitrogenous content of bituminous coal in comperison with brown coal or lignite has been ascribed to the existence of animal matter along with plant residues Chlorophyll which is always associated with green plants, contains nitrogen and can add stable heterocyclic nitrogen containing molecules to coal. Cholorophyll and other porphyrins have been detected in coal. Protein materials such as chitins present in the coating of bacteria, in fungi cells, insects etc. may add nitrogenous substances to coal.

It is generally believed that most of the nitrogen present in humus is protein. The microorganisms which attack proteins in soils contain from 3 to 10% nitrogen. The plant residues usually added to the soil contain 0.32 to 2.4% nitrogen whilst the nitrogen content of soil humus varies from 1 3 to 5 6% showing an enrichment of protein in humus of the soil as a result of carbohydrate decomposition. Microbiologists postulate that the major source of protein in humus is the microbial body cells.

Carbon/nitrogen ratio of coal

The carbon/nitrogen ratio of peats varies from 30.8 to 40. With brown lignite the carbon/nitrogen ratio varies from 30.9 to 127. A sample of lignite containing more sulphur, that is, an acidic coal, showed a carbon/nitrogen ratio of 211. The black lignites have carbon/nitrogen ratios varying from 16.6 to 32. The semi-bituminous coals possess carbon/nitrogen ratios varying from 43.2 to 80 whilst sub-bituminous coals have carbon/nitrogen ratios ranging from 64 to 148. Bituminous coals have carbon/nitrogen ratios varying from 37 to 78, whilst anthracite coals show a carbon/nitrogen ratio, in most cases, of 100 or more.

It is well-known that soot is richer in nitrogen than coal from which it is derived and many samples of domestic soot have carbon/nitrogen ratios as in humus of soils, that is, approximately, 10, and soot collected from kitchen chimneys shows carbon/nitrogen ratio of about 13. The carbon/nitrogen ratio of low moor-peat is about 15.

We are trying to establish that all materials which burn or can be oxidised are capable of being used as agents for nitrogen fixation in soils or other solid surfaces. Composts as prepared at present burn readily and they supply nitrogenous matter to the soil.

Is coal or petrol or mobil oil an inert matter ? They burn readily in air but seem to be oxidised at the ordinary temperature on the soil surface with difficulty, and that is why the nitrogen fixation is a slow process.

Are death and dehydration connected phenomena ? Glucose, cane sugar, starch, cellulose and lignin, formed in the plants, are less and less hydrated as the molecular weight increases. Moreover, the nitrogen content of the plants decreases with increase of lignin, i.e., ageing.

Both animal and plant materials can be used as nitrogenous manures in the soil. A tree is a living thing, so are fungi, algae, bacteria, protozoa etc. They are rich in nitrogen and can serve directly as nitrogenous manure when decomposed in the soil as blood or other protein materials with carbon/nitrogen ratio smaller than 10. On the other hand, plant materials have carbon/nitrogen ratio greater than 10 and hence they not only add the small amount of nitrogen they contain but can fix atmospheric nitrogen and add humus to the soil.

The legumes are an interesting group, because they are both plant and bacterial products and hence, perhaps, intermediate between ordinary plant materials and bacteria. Their carbon/nitrogen ratio varies from 10 to 13 or more according to maturity and the amount of nodules present at the roots. They fix very little nitrogen even when mixed with soils and they have small residual effect. Plant materials with carbon/nitrogen ratio greater than 20 can fix nitrogen and increase humus for more than one year and hence possess residual effect longer in the soil than legumes.

Coal and petrol are certainly mixtures of vegetable and animal matters of which the decay is partially or completely stopped. It

is stated in Waksman's "Humus" that peat contains carbohydrates. We have observed that all carbohydrates can fix atmospheric nitrogen and increase humus, and hence the carbohydrate in peat should be able to fix nitrogen in soil. On the other hand, the carbon and hydrogen of the anthracite coal may be very inert at the ordinary temperature towards atmospheric oxidation and may not be able to fix nitrogen easily. Is it possible to measure the inertness of a combustible matter by its inability to fix nitrogen ? There is no doubt that anthracite coal is less hydrated and contains smaller amounts of oxygen and nitrogen than coals of other ranks.

The urea-formaldehyde polymers when added to the soil may behave as moderately quick acting manures and will be certainly less quick acting than urea because of the presence of the carbonaceous substances derived from formaldehyde. If the nitrogenous substance has to remain in the soil for more than 2-3 months, urea-formaldehyde polymers should behave better than urea or ammonium sulphate alone. In case of sodium or potassium nitrates there is not only leaching more than in ammonium sulphate, but in our soil which has already a tendency towards the alkaline side, more alkalinity is produced and may not be, therefore, suitable for our soils.

Sir John Russell has reported that Hartley and Greenwood, (Emp. J. Expt. Agric 1933, **1**, 113) using one ton of farmyard manure per acre, obtained beneficial results very much better than an equivalent mixture of artificial manure in Nigeria. Moreover, Tempany and co-workers (Emp. J. Experimental Agriculture 1949, **17**,145) have observed that ammonium sulphate renders no good to crops in stations in Malaya having 85″ rainfall; but farmyard manure and other forms of organic substances produce good results.

Elements present in plants and coals

According to Professor G. Bertrand , a flowering lucerne plant contains the following elements :—

Carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, silicon, calcium, magnesium, potassium and sodium varying from 45.37 to 0.157% ; whilst the following elements are present in smaller amounts ranging from 0.0036 to 0.0000027%: iron, aluminium, boron, copper, zinc, manganese, fluorine, titanium, bromine, nickel, molylednum, iodine and cobalt. Moreover, V. M. Goldschmidt and others have reported the presence of the following elements in coal :—

Carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, silicon, calcium, iron, manganese, sodium, potassium, titanium, zirconium, zinc, lead, cadmium, copper, gold, silver, vanadium, beryllium, germanium, nickel, barium, gallium, strontium, boron, scandium, yttrium, lanthanum, cobalt, molybdenum, uranium, arsenic, antimony, tin, iodine, bismuth, rhodium, palladium and platinum.

Elements present in soil

A fertile soil contains the following :—

Carbon, hydrogen, nitrogen, oxygen, phosphorus, potassium, calcium, magnesium, sodium, boron, copper, iron, manganese, zinc, cobalt, aluminium, titanium, molybdenum, chlorine, fluorine, iodine, sulphur and silicon. It is clear that for the healthy growth of a crop the soil must contain those elements which form essential ingredients of plant life.

From ancient times plant materials have been partially decomposed in heaps or in pits and converted into composts which are added to the fields as manure. The aim of composting is to conserve the nitrogen present in the plant materials and add it to the soil with about 10 times its weight of carbon in the form of humus which also contains most of the mineral matters present in the plant residues along with micro-organisms.

Since 1935, Dhar (Presidential address, National Academy of Sciences (India) 15th January (1937)) has emphasized that the direct addition of plant materials to the fields before composting is more beneficial to crops, because the energy materials like carbohy-

drates, celluloses, lignin, fats etc., when added to the soil, are partially oxidised and in this process nitrogen of the air is fixed. The value of the plant residues when added directly is due not only to their nitrogen content but also to the nitrogen fixed from the partial oxidation of their carbonaceous constituents. Hence much more humus (which is a combination of protein with lignin or cellulose or carbohydrate mixed with micro-organism) is formed and added to the soil when plant materials are mixed with the soil direct instead of their addition after composting elsewhere. The method of direct addition of plant materials to soils without composting has been adopted in farms in Pennsylvania and California, U. S. A. The citrus fruit industry in Palestine is utilising the direct addition of fruit and plant residues to the soil under the advice of Dhar in enriching the field

The chief artificial fertilisers used in industrially advanced countries are potassium salts, phosphates and ammonium salts, urea and nitrates, and for acid soils, calcium carbonate It is clear that the above fertilisers do not supply all the materaials required for the healthy growth of a plant. On the other hand, plant residues when added directly, or as compost, supply all the materials needed for plant growth. Dhar and co-workers have shown that carbohydrates, celluloses, lignins and fats act as marked negative catalysts in the oxidation of proteins and ammonium salts or urea to nitrites and nitrates. Hence the proteins added along with plant materials liberate nitrate much more slowly for the benefit of the crop and for a longer period than ammonium salts or urea. The slow liberation of nitrates from humus decreases the chance of leaching away of nitrates from soil. It has been established in Allahabad that when 100 lbs of nitrogen are added to soil in the form of ammonium salts, 60 pounds are lost as nitrogen gas in three or four months without benefit to the soil or the crop/chiefly due to the formation and decomposition of the unstable substance, ammonium nitrite. Proteins also undergo oxidation and partially lose their nitrogen but in the pressence of carbohydrates, celluloses, lignin and fats, the loss is slowed down and hence the crop can absorb the nitrate formed slowly for a longer period.

Nitrogen fixed with coal

We have observed that peat, lignite and bituminous coal when mixed with soil in a very finely divided condition are slowly oxidised and in this process fixation of nitrogen takes place. The amount of nitrogen fixed is greater in sunlight than in the dark. The estimated total nitrogen capital of the world peat and lignite is 47350 million tons. Moreover, the carbonaceous compounds present in coal are more inert than those existing in fresh plant materials, and hence, when finely divided coal is added to the soil, the available soil nitrogen is not readily converted into microbial proteins as with freshly added plant residues. Hence finely divided coal can be mixed with soil and crops can be grown almost immediately without giving any time interval which is needed when plant materials are added directly to the soil.

The growing of paddy and wheat has been found to be benefitted in our experiments by the addition of finely divided lignite and bituminous coal, which add nitrogenous manures and minerals needed for the growth of crops.

It is estimated that the nitrogen content of the humus in the top one foot of the cultivated lands of the world is 40000 million tons. The amount of nitrogen fixed in all the nitrogen industries of the world was 3.54 million tons in 1937. Hence the nitrogen still present in the world soils in the first foot from the top is 11250 times greater than the yearly nitrogen production. It is no wonder, therefore, that only 3 per cent of the world crop yield has been attributed to artificial nitrogenous manures in the last British Association meeting and reported in 'Nature', 1949 vol. 164, No. 4171, page 597, as follows :—

> "At present only some 3% of the world food production can be attributed to the use of nitrogenous fertilizers. To raise the food by 10 %, that is to say one hundred million tons, involves a fourfold increase in supplies of fixed nitrogen at an approximate capital cost of £ 1,50,00,00,000. This would take a minimum of 15 years to achieve."

It is interesting to note that even in the highly industrialized countries, the amount of nitrogen added per acre of land before the second World War, was much less than the nitrogen requirement of even one crop per year as shown below in pounds of nitrogen added per acre of land under cultivation :—

Belgium (28.5), Holland (24.8), Germany (15.6), Denmark (10.3), Norway (6.0), Sweden (5.24), Italy (4.3), France (4.0), Great Britain (2.5), U. S. A. (1.36), Poland (0.73) and Hungary (0.15).

Summary and Conclusion

(1) Ammonium sulphate and ammonium phosphate lose the majority of their nitrogen content as nitrogen gas even in two months after their addition to the soil. With ammonium nitrate, ammonium tartrate, ammonium oxalate and ammonium citrate, urea, hippuric acid, gelatine, oilcake and blood, the loss is less within the same period. With oilcake containing fat, the loss is the least.

(2) With nitrogen rich compounds having a carbon/nitrogen ratio of less than 10, small quantities of humus are added to the soil and there is rapid loss of nitrogen in the gaseous state although they are quick acting nitrogenous manures.

(3) With plant materials, farmyard manure, cowdung, straw etc., with carbon/nitrogen ratio greater than 10, when added to the soil fixation of atmospheric nitrogen and humus formation take place and the addition of humus is much greater than when such substances are added after composting them elsewhere. It has been observed that the greater the carbon/nitrogen ratio of the starting material, the greater is the nitrogen fixation and increase of humus. This is the chief source of soil nitrogen.

(4) Much more nitrogen is fixed in the arable soils of the world by absorption of the solar light per year than the nitrogen fixed in all industrial operations.

(5) Marked nitrogen fixation and humus formation take place both in light and dark under completely sterile conditions with cowdung, leaves of Neem plants (Melia Azadiractta Lina) and wheat straw although the process is slower than in unsterile state.

(6) The efficiency of nitrogen fixation in light in the presence of calcium carbonate with a culture of Azotobacter fed with mannitol is appreciably greater

than in the dark due to the absorption of light by calcium carbonate although the amount of carbon oxidised in light is slightly less than in the dark in some experiments

(7) Soil humus formation and nitrogen fixation also take place with soluble carbohydrates, glycerol and fat

(8) Nitrogen fixation and humus formation on adding organic matters are quicker and greater with sandy soils than in clay soils

(9) There is no decrease of available nitrogen in tropical soils on adding sugars, starch or glycerol although the bacterial population markedly increases

(10) There is an initial decrease of available nitrogen with celluloses, lignins and fats when added to the soil although there is increase of total nitrogen There is also increase of bacterial population with these carbonaceous compounds

(11) The greater the fixation of nitrogen and humus formation in the soil the greater is the residual effect of a manure

(12) Humus liberates nitrates more slowly than ammonium salts and other quick acting manures and benefits the crop for a longer period This explains why the nitrogen status of a soil is not improved without the addition of carbon compounds

(13) The percentage of nitrogen in humus of tropical soils is greater than the percentage of nitrogen in soils of temperate countries Acid soils have higher and alkaline soils lower carbon/nitrogen ratios than normal soils

(14) Peat, lignite, brown coal bituminous coal and anthracite coal have higher carbon/nitrogen ratio than normal soils The higher the rank of the coal the greater is the carbon/nitrogen ratio except lignite which usually contains less nitrogen than bituminous coal

More acidic coals like acid soils have greater carbon/nitrogen ratios than less acidic coals —

(15) Considerable quantities of humus are present in peat, lignite and coal These materials improve crop production by their slow liberation of nitrate and fixation of atmospheric nitrogen These are also beneficial to alkaline soils

(16) Colloidal carbon is present in humus and coal and this causes the black colour

(17) The same elements which are present in plants are also present in coal

(18) The method of direct addition of plant materials without composting is easier and more profitable as there is nitrogen fixation and more humus formation than composting and has been adopted in Pennsylvania and California, U S A and by the citrus fruit industry in Palestine

(19) The estimated total nitrogen content of the world peat and lignite is 47350 millions of tons. The nitrogen content of the humus in the first foot of the arable lands of the world is believed to be 40,000 million tons and the world production of fixed nitrogen in factories was 3 54 million tons in 1937, that is, the soil nitrogen is 11,250 times greater than the fixed nitrogen production per year.

(20) Only three per cent of the world food production has been attributed to artificial nitrogenous manures.

(21) The pounds of nitrogen added per acre of land under cultivation varies from 0,15 in Hungary to 28.5 in Belgium and is much less than that required for the production of one crop per year.

Corrigendum slip of Part 2, Section A, Vol. 18, 1949

CORRIGENDUM

In my paper, "Determination of Elastic Constants of gels by Ultrasonic Method," the rise of amplitude after the second minima is due to the transmission of sonic energy directly. At angles greater than 70° this direct transmission starts taking place. Figures 4-7 needed this explanation.

ARVIND MOHAN SRIVASTAVA

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART II] SECTION A [VOL. 18

DETERMINATION OF ELASTIC CONSTANTS OF GELS BY ULTRASONIC METHOD

ARVIND MOHAN SRIVASTAVA, M. SC.,

Communicated by Dr. R. N. Ghosh, D. Sc., F. N. I., F. N. A. Sc., F. A. S. (America)
(Received on September 8, 1949)

Abstract

The ultrasonic pulse technique developed herein is applied to the determination of the elastic modulii of four gels. The method is entirely new to this line of work and recommends itself because the determinations are quick, accurate and the sample is left undamaged after experimentation. The theories of gel formation have been analysed in brief and attempts are being made to co-relate them with the elastic data obtained.

1. INTRODUCTION

Considerable interest has been shown in the determination of the elastic constants of plastics and other high polymers during the recent years. There is, however, a paucity of published data in the case of gelatinous substances. The importance of this work is three-fold, viz., (1) it provides a basis for comparison, (2) they furnish a scientific criterion for studying the semi-solid nature of gels, and (3) they afford to provide a basis to understand the ultimate mechanical properties of gels.

W. T. Richards[1] and Reggiani[2] have studied the properties of some hydrosols prepared by emulsification. Marinesco[3] has considered the effect of sound waves on gels. He has, however, only considered the absorption of waves and the gradual dimunition of the ampli-

67489

tude of plane waves A year later he used an expression[4] to interrelate the velocity with compressibility and density of the medium in which the plane waves propagate. Bez-Bardili[5] determines the velocity of sound waves in solids and relates them to their elastic constants. These attempts make it apparent that the importance of ultrasonic methods have been under-rated by the colloid chemists. In this paper it is, therefore, intended to initiate the supply of data that might enable them to look into the problem from a totally neglected angle

2 EQUIPMENT

The experimental method is an adaptation of the pulse technique which has been described by Pellam and Galt[7] and by Teetar[8] originating in the work of Massachusetts Institute of Technology Radiation Laboratories. The complete equipment consists of four parts (units) linked together as shown in the schematic diagram, Figure 1

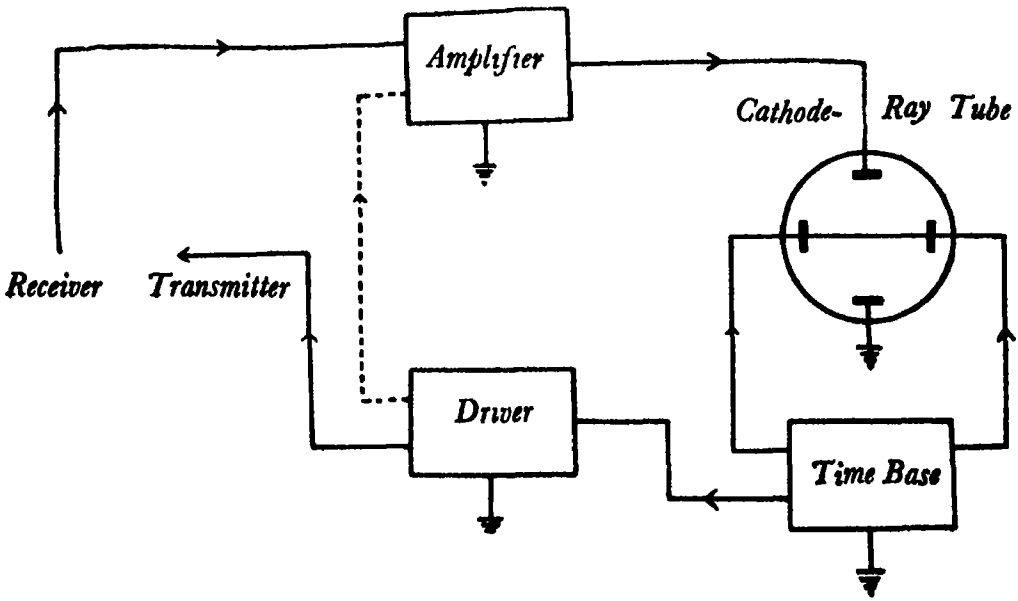


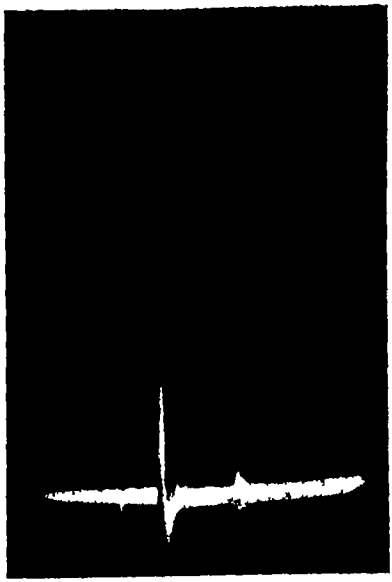
Fig. 1. Block diagram of the equipment.

The Time Base controlled by the alternating current supply mains triggers the Driver unit which supplies electrical impulses to the Transmitter. Thus the equipment operating from a normal 50 cycles per second A. C. mains transmits 50 pulses per second. We now

proceed to consider the transmission of a single pulse at 2.5 Megacycles per second.

The Time Base applies a rapidly changing potential to the X plates of the cathode ray tube so that the cathode ray tube spot moves at a constant velocity across the screen from left to right. Just after the start of the time-base stroke the Driver Unit is triggered by the former and applies a short pulse of energy at the desired frequency of 2·5 Mc/sec. to the Quartz Transmitter; a fraction of this energy is fed directly to the Y plates of the cathode ray tube. Thus the spot moving from left to right across the screen is deflected vertically at the instant of transmission.

Electrical energy supplied to the transmitter is converted into a pulse of 2·5 Mc/sec. supersonic energy which is propagated through the sample under observation, reconverted into electrical energy by the receiver, and this transmitted energy is applied to the Y plates



Photograph 1. Showing the transmitted pulse amplitude.

of the cathode ray tube. The spot is therefore, deflected vertically again. The velocity of the spot as it moves across the cathode ray tube screen from left to right is adjusted so that the vertical deflection occurs

at the right side of the trace. The two vertical deflections are shown in photograph 1.

Conversion of electrical energy to supersonic and vice-versa is affected by the piezo-electric action of a 2 centimetre diameter, 2.5 Mc/sec., X-cut quartz disc fixed to the ends of two cable heads or ends. Both the sides of these quartz discs are thinly silver plated;

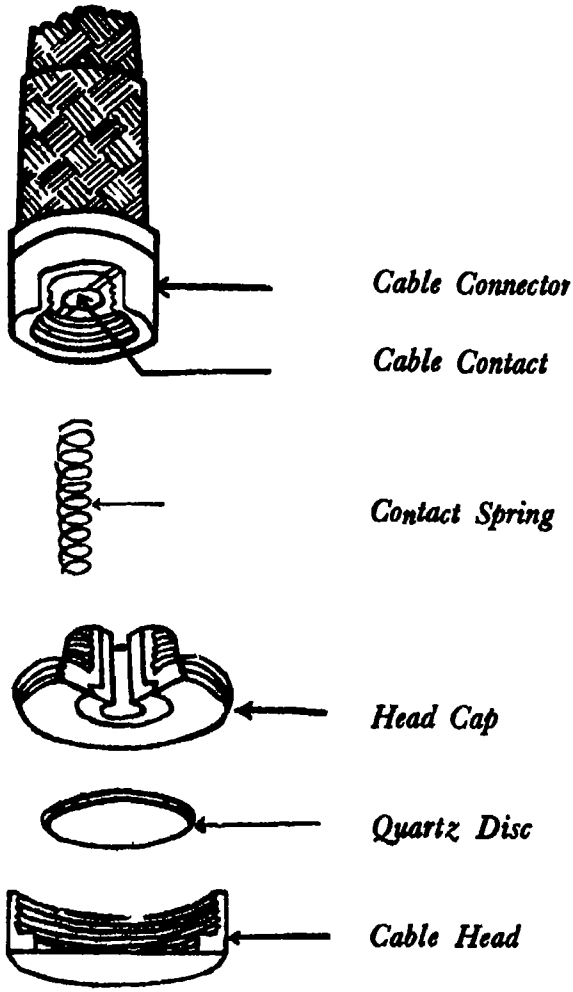


Fig. 2. The assembly and housing of quartz crystal.

contact between the upper surface of the disc and the central conductor of the cable is affected by a spring located in the head cap. The

heads each complete with a quartz disc, head-caps and contact springs are attached to the co-axial concentric cables. Care is taken to ensure that the contact springs are free to slide in the head-caps, and that they press firmly against the recessed cable contacts. A detailed sketch of the whole assembly is seen in Figure 2.

A key is used with which the head-cap may be removed in case it be necessary to examine or replace the quartz disc. The quartz disc and the inner surface of the head should be clean and free from grit. After supplying two or three drops of light machine oil to the inner side of the head the quartz disc is inserted and pressed lightly into position; the head-cap is screwed tightly into position; and the contact spring replaced.

In the apparatus a frequency selection switch is provided on the right side of the panel in front. This selects the output frequency of the transmitter. It consists of the multiway switch introducing various inductances in parallel with the capacity of the transmitter lead (earth) and the crystal. The available frequencies are 2·5 Mc/sec. 2·25 Mc./sec., 1·25 Mc./sec., and ·625. Mc./sec. , and X (mixed frequency). In each inductance there is an adjustable core which requires adjusting if the length of the transmitter lead is changed for any purpose, but otherwise should never be changed.

It is not advisable to lay down rigid rules for the selection of appropriate frequency for any given application, as experience has always appeared to be the best guide. The type of the material often is the determining factor, as for example 2.5 Mc./sec, is suitable for most steels, while for copper this would be too highly attenuated. In the latter case .625 Mc./sec. is more suitable. The position X allows a mixed frequency to be generated and the highest which will penetrate the material in question and can thus be directly seen on the cathode ray tube screen.

Surface conditions of the test sample should be as good as practice will allow, but difficulty arises in case of gelatinous substances which are unrigid and uneven. If there is insufficient sensitivity for this reason the amplifier sensitivity can be sufficiently increased by inserting a plug-in filter in parallel with the receiver.

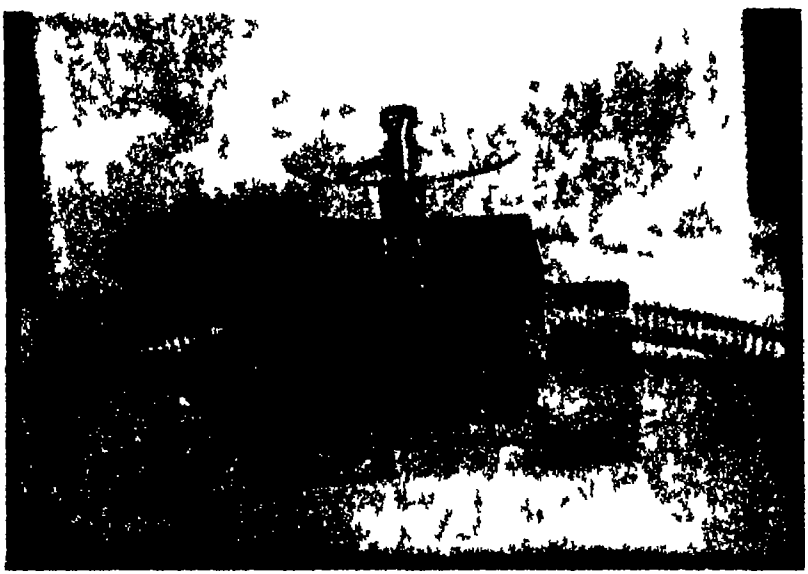
The frequency of this plug-in filter is the same as that of the transmitter

The two techniques available have been suggested by Bar and Walti [8] and by Bez Bardili[4] The mechanical wave set up by the quartz is impinged upon a slab of the material held normal to the direction of propagation of the wave and the energy transmitted is detected by the receiver quartz diametrically opposite to the previous one The generator, the sample of gel and the detector are immersed in a liquid bath to avoid the extreme mismatch of accoustic impedance at the solid-gas interface

While the two quartz are kept fixed in the two slots in the two opposite walls of the liquid container (photograph 2), the test sample of the gel can be rotated in a vertical plane, changing the angle of incidence of ultrasonic waves on the slab This angle of rotation can be measured on a graduated discover which a pointer moves

3 THEORY AND TECHNIQUE

In any isotropic media two types of deformations are exhibited on the application of a stress These are the two well known states of



Photograph 2. Showing the experimental cell

extension and shear The Young s modulus F expresses a resistance to tension and shear modulus S expresses the resistance to shear In the first type of deformations σ the Poisson s ratio is a constant ratio of the cross-sec ional contraction to the elongation in length A re ation bet ween these three is given by

$$F \quad 2(1 + \sigma) S \tag{1}$$

Sound waves that are propagated in a solid take up two velocities depending upon the two deformations ass ciated with them The waves in the case of a simple shear are called shear transverse or rotational ones and their velocity is given by

$$V \quad \sqrt{\left(\frac{S}{\rho}\right)} \tag{2}$$

where ρ is the density of the gel In the deformations of an extension the vibrations are called dilatation longitudinal or irrotational and their velocity is given by

$$V = \sqrt{\left(\frac{(1 \quad \sigma)}{\rho\ 1 \quad \sigma} \frac{F}{1-2\sigma)}\right)} \tag{3}$$

also

$$\sigma = \frac{k \quad 2}{2\ k \quad 1} \tag{4}$$

where,

$$k = Ve/V \tag{5}$$

Thus a knowledge of Ve and Vs enables us a determination of σ, E and S From these one can determine the compressibility m The Bulk modulus of elasticity is

$$K \quad \frac{E}{3(1-2\sigma} \tag{6}$$

and knowing that $m = \frac{1}{K}$ we can calculate m

The method used herein is based upon the variation of the amplitude of the transmitted energy with the angle of incidence of the ultrasonic beam on the slab of jelly Since the velocity in

solid is greater than that in the liquid the wave-trains are refracted away from the normal and the indices of refraction for the two waves are,

$$\left.\begin{aligned} n_l &= \frac{\sin\theta}{\sin\theta_l} = \frac{V_x}{V_l} \\ n_s &= \frac{\sin\theta}{\sin\theta_s} = \frac{V_x}{V_s} \end{aligned}\right\} \qquad (7)$$

where V_x is the velocity in the tank liquid.

As θ increases θ_l also increases so that at a value θ_1 of θ, $\theta_l = 90°$, the dilatation waves are totally reflected and there is a pronounced minimum in the intensity as well as the amplitude of the transmitted

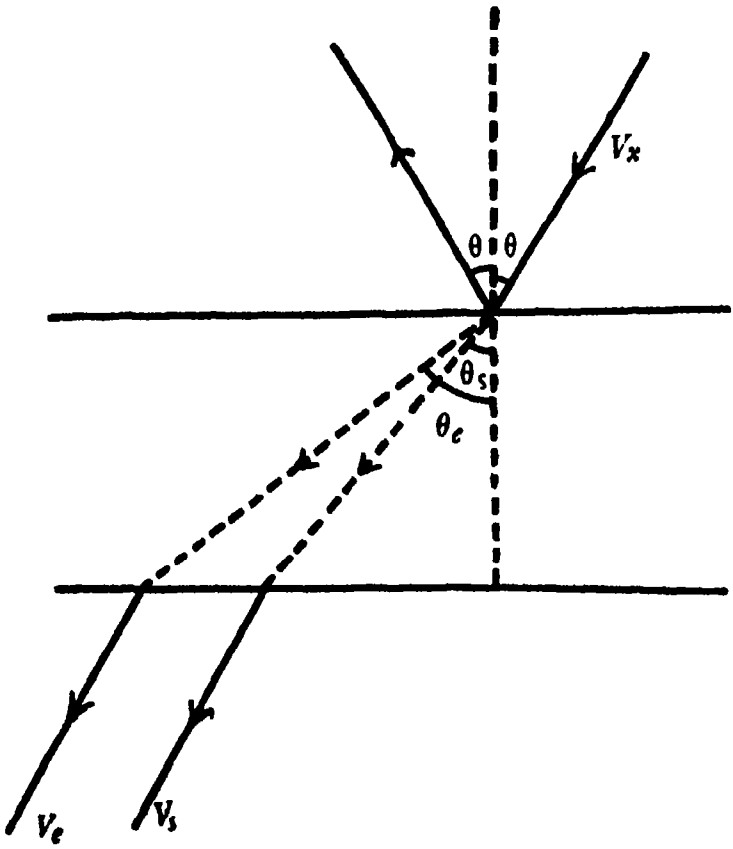


Fig. 3. Showing the various wavetrains.

energy. As θ goes to a further value θ_1, $\theta_2 = 90°$ and the shear waves are totally reflected, then at θ_1 and θ_2;

$$\left.\begin{aligned} V_1 &= V_s/\mathrm{Sin}\,\theta_1 \\ V_2 &= V_s/\mathrm{Sin}\,\theta_2 \end{aligned}\right\} \qquad (8)$$

The amplitudes of the transmitted wave are shown in photograph for a single gel at an angle of incidence other than that at the critical angle. The first vertical maxima shows the start of the pulse, the second and largest amplitude is the magnitude of the transmitted wave and the third maxima to the extreme right is due to reflection of the wave from the front and back surfaces before detection. On rotating the slab of gel the second maxima diminishes twice as the two wave-trains are totally reflected respectively

The above technique has been adopted in my work because of several definite reasons, the main being that; no extensive preparation of the gel sample is needed, the sample thickness is immaterial, the sample is not damaged during the process, evaluations are simple easy and accuate and no involved calculations are necessary.

4. Results

To test the accuracy of the method a few determinations were made with substances whose elastic constants are well known. The results so obtained show that the method is quite safe for application and the accuracy is quite satisfactory. Table 1 shows the values of the angles observed and the velocities of the two wave trains computed therefrom. Figs. 4 to 7 indicate the angles observed when the total reflection of the waves occurs. The two dips correspond to the values θ_1 and θ_2. Table 2, gives the values of the Poisson's ratio, the refractive indices and the ratio k. The third table presents the elastic constants for the four gels that have been studied here.

For the purposes of these calculations the velocity of waves in the tank-liquid water, is taken to be $1{\cdot}55.10^5$ cms./sec. All the values of the velocity are expressed in centimetres per second. Values of E and S are given in dynes per square centimetre, that of m is given in reciprocal of the above.

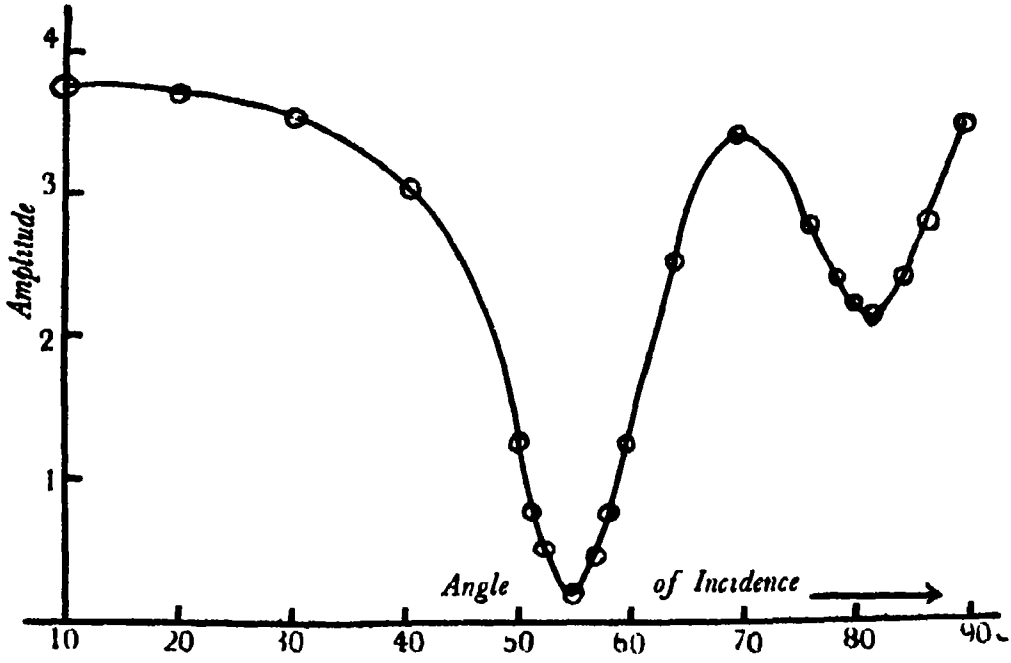


Fig 4 Showing the variation of amplitude of transmitted wave in Silica Gel

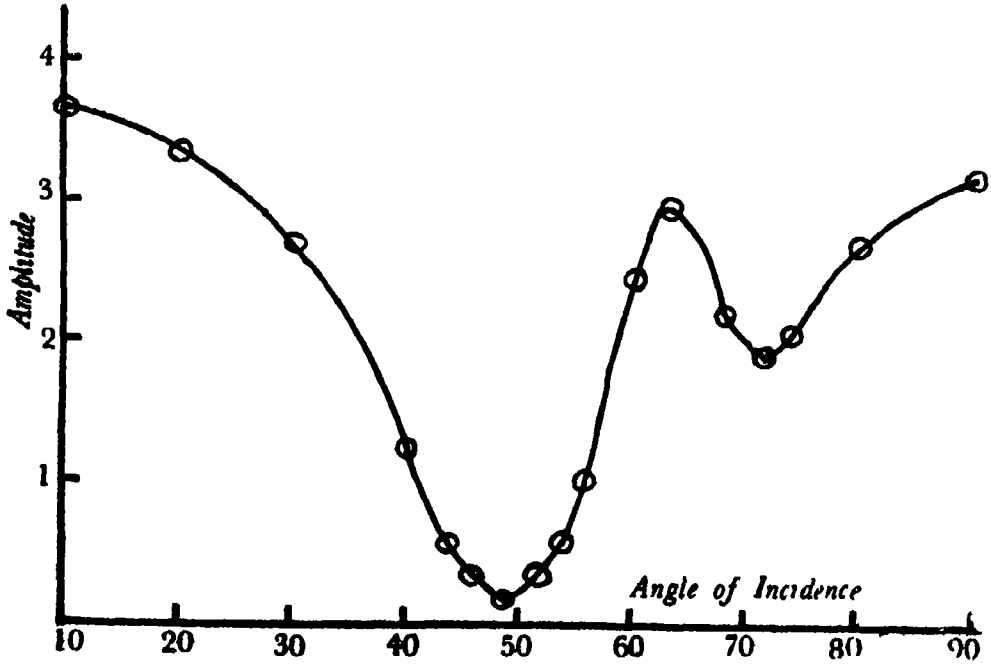


Fig 5 Showing the variation of amplitude of transmitted wave in Barium Sulphate Gel

Fig 6. Showing the variation of amplitude of transmitted wave in Iron Silicate Gel 1

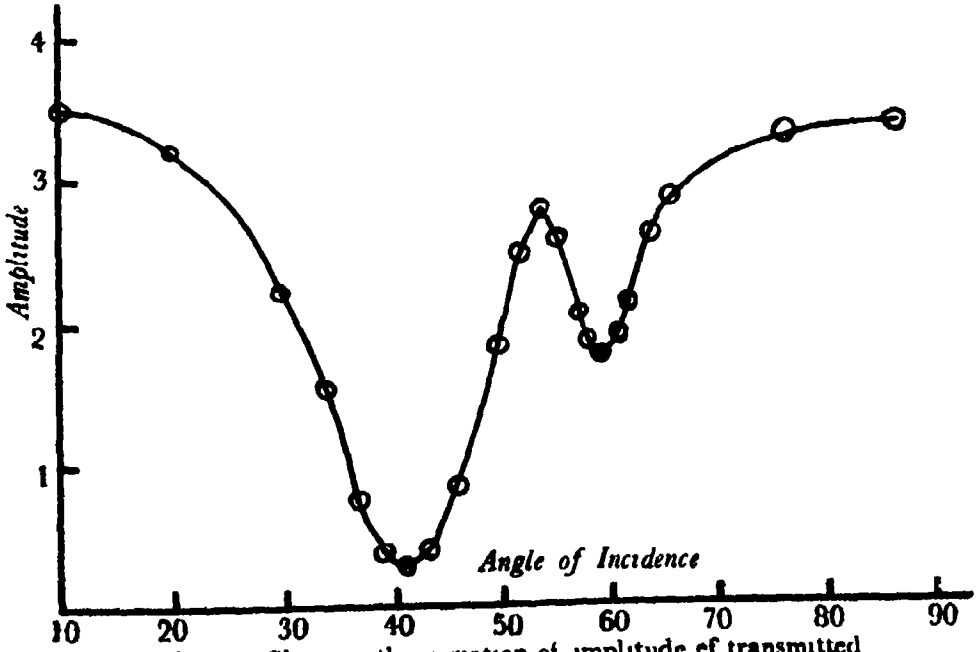


Fig. 7. Showing the variation of amplitude of transmitted wave in Iron Silicate Gel. 2.

Table No. 1.

No.	Gel	ρ	θ_1	θ_2	Ve	Vs
1.	Silica, SiO_2	1·14	53·5°	81·0°	$1{\cdot}85.10^5$	$1{\cdot}57\ 10^5$
2.	Barium Sulphate	1·22	49·0°	72·0°	$2\ 06.10^5$	1·65.10
3.	Iron Silicate 1.	1 27	45·0°	62 0°	$2\ 15.10^5$	$1\ 70.10^5$
4.	Iron Silicate2.	1 35	41·0°	59·0°	$2{\cdot}25.10^5$	$1\ 74.10^5$

Table No. 2.

No.	Gel	n_1	n_2	k	$-\sigma$
1.	Silica, SiO_2	.81	.98	1.19	.63
2.	Barium Sulphate	.74	.95	1.24	.44
3.	Iron Silicate 1	69	.89	1.26	.35
4.	Iron Silicate 2	.66	.86	1 29	.22

Table No. 3.

No.	Gel	E	S	K	m
1.	Sinca SiO_2	$2\ 01.10^{10}$	$2\ 84.10^{10}$	$2\ 93.10^9$	$3{\cdot}41.10^{-10}$
2.	Barium Sulphate	$4\ 01.10^{10}$	$3{\cdot}22.10^{10}$	$7{\cdot}95.10^9$	$1{\cdot}26.10^{-10}$
3.	Iron Silicate 1	$4{\cdot}79.10^{10}$	$3{\cdot}67.10^{10}$	$9{\cdot}40.10^9$	$1{\cdot}06.10^{-10}$
4.	Iron Silicate 2	$5{\cdot}18.10^{10}$	$4{\cdot}09.10^{10}$	$11{\cdot}46.10^9$	$\cdot 88.10^{-10}$

5. Discussion

The colloidal state of matter shows certain interesting and distinctive properties that are absent in the two constituent phases themselves. A gel represents a specific type of colloid wherein a liquid is dispersed in a solid dispersion medium. The properties of such a system are therefore naturally perplexing in certain respects. Although a large amount of work has been done on gels there is no agreed view on the mechanism of gel formation. Weimarn[9] holds the view that a precipitate may be crystalline, amorphous, or gelatinous according to the percentage of supersaturation. Bradford[10] is in general agreement with Weimarn and he maintains that the gels have two phases—an ultramicroscopic solid phase soaked in a liquid dispersion medium retained by capillary and molecular forces. Bancroft[11] on the contrary believes that there are other factors besides percentage supersaturation that effect the formation of the nuclei in the gels. It is apparent, therefore, that much further work is needed to elucidiate the mechanism of gel formation to understand properly the semi-solid nature of these substances.

A large amount of work has been done by Dhar[12] who has classified the jellies into three groups. In the first group the particle show some basic network and the jellies are easily formed, more stable like gelatine, agar-agar, soaps, etc. The second group consists of gels formed by the slow coagulation of a sol throughout its entire mass and the particles do not consists of a network. Hydroxides of iron and chromium are members of this class. The substances involved in this class have a marked affinity for water and they are less stable. The third group forms the Weimarn class consisting of substances precipitated very suddenly, they are the least stable.

On accumulation of further data we intend to support one of the above views on the mechanism of gel formation. For the present this paper supplies a new approach to others interested in this line of work.

6. Acknowledgement

I wish to record my sincerest thank to Prof. N. R. Dhar and Dr. R. N. Ghosh who have afforded me encouragement and guidance that enabled me to undertake this work.

References

1. Richards, W. T. — J. Amer. Chem. Soc., 51, 1724, 1929.
2. Reggiani — Competus Rendus, 200, 123, 1935.
3. Marinesco, M N — Comptes Rendus, 194, 1824, 1932.
4. Marinesco, M. N. — Comp es Rendus, 196, 346, 1933.
5. Bez-Bardili W. — Zeits f Phy., 96, 761, 1935
6. Bar and Walti — Helv. Phy Acta., 7, 658, 1935
7. Pellam J. R. and Galt J. K. — J. Chem. Phy., 14, 608, 1946
8. Teetar, C. E. Jr. — J Acc. Soc. Amer. 18, 488, 1946.
9. Weimarn — Koll. Zeit. 2, 199, 230, 275, 301, 326; Suppl. 2 LII; 3, 89, 282, 1908.
10. Bradford — Brochem. J. 12, 351, 1918; 15, 553, 1921.
11. Bancroft W. D. — Colloid Chem., pp. 41.
12. Dhar, N. R. — J. Ind. Chem. Soc., 5, 309, 1928; 6, 587, 1929; 7, 367, 1930; 7, 591, 1930.

ACTION OF LIGHT ON COLOURING MATTERS AND THEIR OXIDATION

By

N. R. DHAR

(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALLAHABAD, ALLAHABAD, INDIA)

Photo-oxidation and photo-decomposition of colouring matters.

In my book 'Chemical Action of Light' (Blackie & Sons. 1931) it was pointed out that the phenomenon of photo-oxidation of organic and inorganic substances by atmospheric oxygen is of common occurrence. In recent years we have carried on systematic work on the photo-oxidation of carbohydrates, celluloses, fats, glycerol, pentosans and other energy materials by air at the ordinary temperature in presence of soil or insoluble oxides, phosphates, sulphates, carbonates etc and have shown that in these oxidations of energy materials, fixation of atmospheric nitrogen takes place, more in light than in the dark. (Dhar. Presidential address, National Academy of Sciences, India. 1935, 1937. *Proc. National Academy of Sciences, India.* **15** (1946), 15. **16**, (1947), 6.)

Dhar and co-workers (*Z. anorg. Chem.* **142**, (1925) 299) have shown that dyes are solutions or suspensions of unstable substances and can be oxidised or reduced. Usually these solutions or suspensions when exposed to light are oxidised by the dissolved oxygen and hence there is a bleaching of the dye on exposure to light. In presence of strong light, specially ultra-violet radiations, some dye solutions or suspensions are actually decomposed and lose colour, just as solutions of ammonium nitrite, potassium persulphate, trichlor-aceticacid etc., are decomposed in light. Even when the dyes are adsorbed on fibres photo-reduction of the dyes by cellulose can take place. Moreover some dyes adsorbed on cellulose also undergo photo-oxidation on the cellulose surface by air.

Most of the dyes do not fade in absence of air and fibre. Wool and silk are found to exert less reducing action on dyes than cotton.

It is well known that substances like ozone, hydrogen peroxide, ammonium nitrite etc undergo thermal and photo-chemical decomposition readily. Similarly explosives which are very unstable substances can also undergo decomposition by increase of temperature or when exposed to light. Dyes like picric acid and Aurantia behave like explosives and fade due chiefly to the breaking of the molecules by light absorption.

On the other hand, most of the basic dyes are free from oxygen and contain several carbon and hydrogen atoms in the molecule and they can behave as reducing agents specially in presence of light. Such dyes can undergo photo-oxidation by the oxygen of the air and get bleached. The basic dyes are less fast to light than acidic dyes which are certainly less reducing in their properties than basic dyes. All basic dyes contain less oxygen in their molecules than acidic dyes. It is generally observed that the presence of unsaturated and conjugate groups is needed for the formation of a dye. But these groups also make the molecules unstable. Moreover, it is well known that the greater the molecular weight of a dye and the greater the number of unsaturated and conjugate groups present, the greater is the depth of its colour. Also the dyes with low molecular weight exist in the molecular condition in solution and are more easily photo-oxidised by air than dyes with larger molecular weights which are either insoluble in water or form colloids and are less liable to be photo-oxidised. It is clear, therefore, that a dye can fade due to the one or more of the following causes:—

(1) Photo-decomposition. (2) Photo-oxidation by air. (3) Photo-reduction by the fibre or mordant.

It appears that with basic dyes photo-oxidation by air is the chief cause of fading. But with acidic dyes containing oxygen atoms in the molecule there is a greater possibility of photo decomposition and photo-reduction than photo-oxidation.

In some cases dyes containing oxygen can undergo decomposition in light by auto-oxidation and reduction just like nitrous acid or benzaldehyde according to the equations:—

$$3\ HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$
$$2\ C_6H_5CHO + H_2O \rightarrow C_6H_5CH_2OH + C_6H_5COOH$$

It is interesting to note that the use of the nitro compounds picric acid and Aurantia containing three and six nitro groups in the benzene nucleus, as dyes has been given up because they are fugitive but they are used as explosives. Aurantia is used as a staining material. Many years ago D. Berthelot and H. Gaudechon [Compt reund **153**, 1220 (1911); **154**, 201, 514. (1912)] studied the photo-decomposition of explosives like powders, cordite, nitro-glycerine etc in amounts weighing from 0.24 to 0.45 gram and observed their rapid decomposition to gaseous products when exposed to ultra-violet radiations. Such decomposition also takes place in visible light at a lower speed. It appears, therefore, that organic compounds and dyes containing several nitro groups in the molecule may undergo photo decomposition and may prove fugitive. Moreover such dyes containing several oxygen atoms in the molecule may also undergo photo-reduction by the fibres or mordants which are generally reducing agents, specially cotton, which in presence of light exerts more reducing property than wool or silk. Hence dyes with several nitro groups are not likely to be commercially successful because of their fugitiveness and instability.

It is generally believed that in photosynthesis in plants the following compounds according to their increasing complexity and molecular weight are produced: —

Formaldehyde—glucose—complex sugars starch—cellulose—lignin.

Formaldehyde, glucose, cane sugar, starch etc. have been found to decompose in light specially ultra-violet, into different gaseous products in absence of oxygen. Dhar and coworkers (Influence of light on some biochemical processes. 1935) have shown that all carbohydrates, fats, organic acids, cellulose and even lignin can undergo photo-oxidation by air and in many cases the nitrogen of the air is also fixed in this process. It appears therefore that organic compounds

can undergo photo-oxidation and photo decomposition specially under strong illumination. The ease of photo-oxidation and decomposition decreases markedly as the molecules become more and more complex. This behaviour is observable with natural and artificial colouring substances. Although they are organic substances and are liable to be photochemically oxidised and decomposed, they resist these processes pretty well because they are usually derivatives of aromatic hydrocarbons and their heterocyclic counterparts have a ring structure. More over, most dyes are of large molecular weights and are eithe insoluble in water or exist in the colloidal condition having large molecular aggregates. Once the colouring matter is adsorbed on the fibre with or without mordants they are usually stabilised perhaps by rendering them as insoluble as possible and forming stable adsorption complexes. In this connection it is interesting to note that the phospho molybdo-tungstic acid lakes formed by adsorbing methyl violet and other basic and cyanin dyes make them more fast towards light. In other words, the greater the stability of the adsorption complex formed with mordants and fibres the greater is the stability towards light

The natural colouring matter chlorophyll A and chlorophyll B containing a large number of carbon and hydrogen atoms and an atom of magnesium would behave as reducing substances like some of the basic dyes and would be liable to photo-oxidation by air. On the other hand, the anthocynin colouring substances notably pelargonidin, cyanidin, peonidin, delphinidin, malvidin, hirsutidin are richer in oxygen than chlorophyll and resist photo-oxidation by air better and are more fast to light than chlorophyll. Similarly the following dye stuffs quercetin, fisetin etc. have been in use as yellow mordant dyestuffs from ancient times. Quercetin is still a valuable dye for wool. Luteolin, another natural flavone dye is being used for producing a fast yellow shade on wool and silk with aluminium or tin mordants. These are more fast as they contain more oxygen than chlorophyll and hence resist photo-oxidation. It is interesting to note that the majority of colouring substances both natural and artificial contain nitrogen which makes the dyes more stable towards photo-oxidation.

Most basic dyes have lower molecular weights than acidic dyes. They contain less oxygen than acidic dyes and hence possess more reducing power and are thus liable to be photo chemically oxidised by air. Cotton being more reducing in its properties than wool or silk, the basic dyes have greater advantage over acidic ones in the dyeing of cotton.

Most of the azo dyes, both basic and acidic have smaller molecular weights than some other more complex dyes and the weak point of the azo dyes is their unstability towards light By increasing the molecular weight of such azo dyes the light fastness increases. Certain groups such as the pyrazolone and nitro or sulphonic groups ortho to the azo links are beneficial to light fastness. Tartrazine, an acidic dye is a bright yellow compound exceedingly fast to light like all pyrazolone colours. Auramine hydrochloride, a basic dye, is one of the most important synthetic dyestuffs and contains no sulphur. As the molecular weight of this substance is not high (303.5), the shade is not fast to light. The well known nitro acidic dyestuff Napthol yellow S having a molecular weight of 392, used in dyeing animal fibres changes colour to a brownish shade when exposed to light. Basic azo dyes such as Bismarck brown can be fixed on cotton mordanted with tannin and tartar emetic but this method is now of little importance. On the other hand many azo dyes having suitably disposed hydroxy or carboxy groups form inner coordination compounds with copper and chromium salts and these are of first importance. They frequently possess very high light fastness as well as good washing fitness. The thiazole acidic dye Primuline (molecular weight 475) and its diazo salts are not light fast.

The simpler basic dyes such as magenta and malachite green are readily bleached by sunlight which is a serious weakness of most of the triphenyl methane group of colouring matters. The molecular weight of magenta is 322.5 and that of malachite green is 364.5. On the other hand the alizarin cyanin dyestuffs such as alizarin cyanin green which is an acidic dye of molecular weight 578 are equal in purity of shade to the triphenyl methane colours and are very much faster to light. It is interesting to note that several triphenyl methane

dyes containing negative substituents are faster than the simpler basic dyes and some of the sulphonated triphenyl colours are of great beauty and are acid dyes suitable for colouring wool but not very light stable.

Some phenyl and toluidine derivatives of rosaniline have yielded well known basic dyes like Victor blue 4R, Night blue and these are mainly used for colouring silk. The shades are good but fugitive to light. The acid dyes obtained from Rosalic acid, aeriochrome azurol B dyes wool a wine red colour and the dye is moderately fast to light. The sulphonated Rhodamines like acid violet 4R or violamine R or violamine 3B are much faster to light than the basic rhodamines. They range in colour from violet to blue and are of considerable value for dyeing of wool or silk. Fluorescein dyes with low molecular weights, although acidic ones, are fugitive towards light. The halogenated fluoresceins are most beautiful artificial dyes but are not light fast. Rose Bengale and erythrosine are of value for sensitizing photographic plates to green and yellow light. These dyes are frequently mixed with the isocyanin dyes for improving their sensitivity towards light. When flavanthrone is treated with alkaline sodium hydrosulphite at 65° a violet blue colouring matter for dyeing cotton substantively is produced. When the dyed fibre is exposed to air the blue colour changes to brilliant yellow by oxidation but the colour is not fast to light. On the other hand, the acid dye Indanthrene golden orange G gives a purple shade on cotton which when oxidised becomes a light fast orange dye. It is interesting to note that the following colouring matters are being used as light filters and for absorbing radiations of different wave lengths in all kinds of optical work : -

Fluorescein, Rhodamine B, Nitroso-dimethylaniline, Triphenyl methane, Methyl violet, Methyl green, Picric acid, Crystal violet, Double green, Violet yellow, Aesculin, Guinea green B extra, Chrysoidine, Eosin, Tartrazine etc. On long exposure to light some of these dyes undergo photo-oxidation or decomposition.

In dyeing by the two famous colouring matters of the ancient world—Tyrian purple and Indigo—oxidation of the colouring matter

by air in presence of light played a very important part. If cotton is continuously exposed to sunlight, it loses strength due to partial oxidation. This is particularly true of curtains, which may appear in perfect condition when hanging at the windows but when taken down may fall apart in spots where sunlight has reached them.

The photo-decomposition of chlorophyll solution was probably first observed by Senebier in 1788. He noted that solutions of chlorophyll in acetone, alcohol, benzene and ether were rapidly decolourised by light in presence of air. Gaffron (Ber. 60 B, (1927) 2229) has shown that under the influence of light a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of chlorophyll. Wurmser (Arch. Phys. Biol. I, No. 3, Sept. 1921) has studied the photo-decomposition as a function of the wavelength of the light used. He found out that the amount of decomposition which takes place depends only on the amount of energy absorbed and is independent of the wavelength. He also concluded that the decomposition is an oxidation process. Chlorophyll is not so susceptible to photo-decomposition in the living leaf as it is in solutions in organic solvents. If water is added to an acetone solution of chlorophyll, a colloidal solution is formed and in this condition the stability of chlorophyll in presence of light is much increased. Wurmser found that addition of very small percentage of colloids such as casein, gelatine, albumin and gum arabic, made a solution of colloidal chlorophyll much more stable in presence of light. The addition of starch had practically no effect on the stability of chlorophyll. As a result of these experiments Wurmser suggested that the chlorophyll in the living leaf is probably protected against photo-decomposition and photo-oxidation by the presence of colloids. Albers (Phys. Rev. **46,** 1934, 336) has shown that the photo-decomposition of chlorophyll increases with increase of temperature. This would indicate that the photo-decomposition of chlorophyll is not entirely photochemical.

Knorr and Albers (*Phys. Rev.* **47,** 1935, 329) have shown that the fluorescence of chlorophyll vanishes as the solutions are bleached and that the chlorophylls and their derivatives decompose under

the action of light in acetone solutions and in an atmosphere of oxygen, carbon dioxide or nitrogen. The relative intensities of the individual absorption bands of chlorophyll change considerably during the photo-decomposition and photo-oxidation but the position of the bands does not shift. It is clear therefore that in the case of chlorophyll there is photo-decomposition as well as photo-oxidation in acetone and alcoholic solutions.

The experiments of Knorr with chlorophyll and its derivatives dissolved in acetone show that these are true cases of photo-decomposition and perhaps photo-reduction also by the reducing substance acetone because oxygen does not help the loss of fluorescence. From theabove observations it is clear that chlorophyll occurring in the state of solution undergoes photo-decomposition, photo-oxidation and photo-reduction more readily than chlorophyll existing in the colloidal state or protected by colloidal substances like casein, gelatine or gum arabic. This conclusion is supported by the observations of Dhar and Bhattacharya (J. Indian Chem. Soc. **4**, 1925, 299) on the bleaching of different dyes in air and sunlight aided by zinc oxide as a photo-catalyst. About forty dyes were investigated and the dyes can be classified according to their bleaching in three categories :—

1. Readily bleached :—Crystal violet, methylene blue, ethyl green, nile blue, azolitmin, aniline blue, nigrosine, gentian violet, malachite green, methyl violet, eosin and fluorescein
2. Not readily bleached: —Indigo-caramine, rhodamine, erythrosine, uranine, acridine red, congo red, aurine, magenta, aniline yellow, methyl orange, purpurin, tropeolin, aesculin, thioflavine.
3. Not bleached :—Alizarin blue, water blue, cupric blue, victoria blue, pyronine, rose bengale, aniline red, auramine, aniline scarlet, theonine, corcus red, rosaniline, acridine orange and acridine yellow.

Among those which are easily bleached are chiefly the basic dyes and which exist generally in the dissolved condition and their

molecular weights are lower than those of acid dyes. The following basic dyes are not much bleached :

Thioflavine, rosaniline, acridine orange, acridine yellow, auramine, magenta, acridine red, pyronine, aurine, rhodamine, erythrosine, victoria blue. Most of these dyes are partially colloidal in water.

The following are acid dyes and exist in colloidal state; these are not very much bleached :—

Alizarin blue, uranine, congo red, aniline red, aniline yellow, methyl orange, purpurin and tropeoline.

The aqueous solutions of substantive dyes tend to be colloidal while those of the non substantive dyes usually give molecular solutions. Benzopurpurin 4B a strongly substantive dye and the isomeric 4 : 4 - diamino 2:2 toluidine analogue, a feebly substantive dye have been found by Robinson and Mill to have complex anions in solution, but those of the substantive dyes are much larger.

The adsorption of a dye by a fibre depends upon the size of the dye particle. If the particles are too small, i.e. if they approach the molecular dimensions the adsorption on the fibre is not much pronounced. On the other hand if the particles are too big, they may not form a uniform layer on the fibre. Hence particles resembling the precipitate condition or those in the dissolved conditions should not make good dyes. Particles of intermediate sizes should form better dyes. This view explains the usefulness of adding sodium salts in dyeing. It has been shown by Dhar and Chatterji (Koll. Z. 1925, **37**, 89) that various sols can be adsorbed by their freshly obtained precipitates. Similarly barium sulphate and other substances can act as adsorbents of colloidal matter. But such precipitates do not show much adsorption for substances in the molecular or ionic condition. It is clear, therefore, that the textile fibres can adsorb dyes in colloidal condition more than those in molecular condition.

Dhar and coworkers (J. Indian Chem. Soc. 6, 1929, 145) have determined the extinction coefficients and decolourisation, energetics

of the photochemical bleaching of Neocyanin (Kodak) by oxygen of air. This colouring matter shows marked light absorption in the red and infra-red side and the velocity of the photochemical bleaching is largest in the regions 3704° A and 8500° A where the light absorption is also maximum. The bleaching is proportional to the square root of the changes in light intensity and the temperature coefficient of bleaching varies from 1.04 to 1.30 and the quantum efficiency changes from 1 to 4 depending upon the wavelength of light.

The bleaching of very dilute solutions of Dicyanin by oxygen of the air in light was also investigated by Dhar and Mukerji (*J. Phys. Chem.* **33**, 1929, 850) The reaction is unimolecular and the temperature coefficient is about unity and the quantum yield varies from 0.5 to 2.0.

The bleaching of Chinaldin cyanin, pinachrome cyanin, lepidincyanin, Pinaverdol in collodion films was investigated by Lasareff (*Ann. Physik* **24**, 1907, 661) and the bleaching has been attributed to the oxidation of the dye by oxygen. From the data of Lasareff, Bodenstein (*ibid.* **37**, 1912, 812) concluded that the quantum yield is much smaller than unity. Apart from this photo-oxidation there is a photo-chemical decomposition of the dye, as well as an interaction of the nitro cellulose of the collodion and the dye in presence of light The temperature coefficient of the reaction is almost unity.

Waviloff (*Z. physik. Chem* **100**, 1922, 266) studied the bleaching of pinaverdol, cyanine, lepidine cyanin and chinaldincyanin in the dark between 60° and 120° in collodion film. It seems that a reaction takes place between the nitro-cellulose and the dyes at this high temperature. There is no bleaching of the solid dye at this temperature interval in the absence of collodion. The temperature coefficient in the thermal process is two.

Weigert (*Z. Physik* **5**, 1920, 410), Predwoditeleff and Netschajewa (*ibid* **32**, 1925, 226) observed that the initial rate of bleaching of these dyes in collodion films on illumination is proportional to the light absorbed when the concentration of the dye is very small. When the concentration of the dye is increased the velocity becomes a periodic function of the dye concentration.

Zchodro (*J. chim. phys.* 29, 1929, 59) has shown that the electric conductivity of the collodion films coloured with cyanin, pinaverdol or pinachrome increases on illumination but no increase is observed when the film has become decolourised. When illumination ceases the electric conductivity gradually decreases.

Chemiluminescence in the oxidation of dyes.

The glow observed when different dyes and organic substances are oxidised by ozone or hydrogen peroxide has been investigated by Dhar and coworkers (Z. anorg. Chem. **173**, 1928, 125) with the following results :—

Dyes.	Solvent.	wavelength of light emitted
Eosin	Methyl alcohol	6020 to 5320 °A.
Uranine	Ethyl alcohol	5860 to 5030 ,,
Neutral red	Methyl alcohol	6050 to 4850 ,,
Rhodamine B	Ethyl alcohol	6170 to 4670 ,,
Thioflavine	Ethyl alcohol	5700 to 4690 ,,
Cartharamine	Methyl alcohol	6650 to 4580 ,,
Rhodamine BJNN	Ethyl alcohol	6190 to 4620 ,,
Erythrosin	Ethyl alcohol	6060 to 5310 ,,
Cartharamine	Ethyl alcohol	6050 to 5860 ,,
Rhodamine	Ethyl alcohol	5910 to 5530 ,,

The foregoing flourescent dyes gave out the best glow amongst the numerous dyes investigated by us. When ozonised oxygen is passed through solutions of the following fluorescent and non-fluorescent substances a glow is also observed but the intensity of the glow is less than that obtained with the first group of fluorescent dyes :—

Methyl blue, alizarin, resorcinol benzene, azure eosin, rose bengale, theonine, methylene blue 2B, chlorophyll, resorcinol succinyl, resorcinolacetonedicarboxylene, gallein, fluorescein alkaline and aesculin.

There are several other dyes in which the glow was less intense than in the two previous groups. We have also observed that several dyes, when oxidised by hydrogen peroxide and ferrous sulphate become luminous. In this case both fluorescent and non-fluorescent dyes when oxidised by hydrogen peroxide and ferrous sulphate give out glow.

It is interesting to note that the glow on the oxidation of dyes is intense when the dyes are fluorescent. The chemiluminescence spectra of Rhodamine B extends from 6170 to 4670°A. and the fluorescent spectrum recorded by Kautsky and Neitzke (*Z. Physik.* **31**, 1925, 60) consists of lines from 6680 to 4400°A. Hence it appears that the chemiluminescence spectra and fluorescent spectra of Rhodamine B are not altogether identical as has been assumed by Kautsky. Numerous fluorescent and non-fluorescent substances give out glow when oxidised by ozonised oxygen or hydrogen peroxide and ferrous sulphate and the glow is intensified by warming the solutions. But the view advanced by Jorissen (*Chem. Weekbend* **1**, 1904, 789) and Moureu and Dufraisse (Reports of Solvay international council of chemistry Brussels, 1925, page 524) that slow oxidation is always accompanied by luminescence is not correct because there are numerous substances which can be oxidised either by oxygen or hydrogen peroxide or ozone and do not emit a glow. The intensity of the glow given out in the oxidation of dyes becomes less with the increase in the concentration of the dye. The late Professor J. Perrin reported (*Ann. d. Phys.* (9) **10**, 133 ,1918) *Compt. rend* **177**, (1923, 714) that the intensity of fluorescence of substances decreases considerably as the solution is concentrated. He also advanced the view (*ibid.* **178**, 1924, 1401) that the phenomenon of fluorescence is caused by the decomposition of the molecules of the fluorescent substances. In other words Perrin included fluorescence in the domain of chemiluminescence.

Wood (*Phil. Mag.* (**6**), **43**, 1922, 757) supported the hypothesis of Perrin from his experiments on rhodamine.

It is observed that an aqueous solution of aesculin in contact with the atmosphere loses about 60 per cent of its fluorescing power when exposed in a glass tube to the radiations of a mercury arc for one hour. The active wavelengths are longer than 3300°A. in this case. In an evacuated glass tube the fluorescence power remains constant during an irradiation period of 30 hours. In a quartz tube evacuated and sealed off, the intensity of the fluorescence decreases after 2 hours to 19 per cent of its initial value. This loss is due to the photo-decomposition of aesculin by the absorption of the mercury lines of wavelengths below 3300°A. As a general rule it can be stated that the organic and inorganic fluorescent materials are much less subjected to fading if they are carefully protected from oxygen and in some cases from water vapour.

It is generally found that the closed ring structure of the dye is associated with the appearance of fluorescence. Only 85 out of the 1450 dyestuffs listed in the colour index give out fluorescent light. None of the large group of dyes included in the azo dyestuffs is fluorescent. The most brilliantly fluorescent compounds flourescein eosin and rhodamine belong to the xanthene group. Euchrysine, trypaflavine, choriphosphine in the acridine group, primulin and thioflavine in the thiazole group, magdala red and safranine in the azine group and some indanthrene dyes show marked fluorescence and they all contain a closed ring structure. On the other hand, the open bridge compounds like auramine, malachite green or crystal violet are not fluorescent.

It seems that although the closed ring structure adds more stability towards photo-chemical oxidation of the dyes than the open chain compounds like malachite green but the fluorescent dyes are liable to be photo-chemically oxidised by oxygen of the air and in this respect they behave like chlorophyll.

Weigert (*Z. Physik.* **10**, 1922, 349), McLennan and Miss Cale (*Proc. Roy. Soc.* **102** *A*, 1922, 256) Miss Kearney (*Phil. Mag.* **47**,

124,48) Pringsheim (*Z. Physik* **10,** (1922),176) and Chakravarti and Dhar (*Z. anorg. Chem.* **142,** 1925, 299) and Beese and Marden (*J. optical Soc. Am.* **32** (1942), 317) showed that the bleaching of fluorescent substances is not caused by fluorescence but is due to to the photo-oxidation of the organic compounds by oxygen of the air. Hence the bleaching of the dyes on exposure to light is in most cases due to photo-oxidation and in some cases when the illumination is intense the photo-decomposition of dye can take place. This phenomenon of fading has nothing to do with the fluorescence of substances.

We have shown that the solutions of ammonium nitrite, when exposed to light and air in the presence or absence of substances like silica, zinc oxide or titanium dioxide undergo two types of changes, photo decomposition and photo oxidation according to the equations;

$$NH_4\ NO_2 \rightarrow N_2 + 2H_2O$$

and $$NH_4\ NO_2 + O_2 \rightarrow 2NH_4\ NO_3$$

Many dyes also can undergo photo-oxidation and photo-decomposition like ammonium nitrite, the difference being that in the case of ammonium nitrite the photo-decomposition is more pronounced than the photo-oxidation, while with the dyes photo-oxidation is more pronounced, specially with basic dyes, than photo-decomposition. It is clear, therefore, that the phenomenon of fluorescence of colouring matter cannot be included in the realm of chemiluminescence.

Dyes as Photo-sensitizers and Desensitizers.

In 1873 Vogel discovered accidently that photographic plates stained with a yellow dye showed a maximum sensitivity to light in green instead of the blue region of the spectrum. Becquerel in 1874 found that chlorophyll had the same effect. In 1875 Water-house observed that eosin is a powerful sensitizer for green and yellow light. The associated dyes rose bengale and erythrosin are still used for this purpose.

It is well known that at present colouring matters are extensively used in increasing the sensitivity of photographic plates. It has been observed that a maximum of sensitiveness corresponds to a maximum

light absorption. The photographic plates become sensitive to the rays absorbed by colouring matters. But all coloured substances cannot act as optical sensitizers. In order that a coloured substance may be active, it is necessary that it should be absorbed by the silver halide and must be able to exert a reducing action on the silver salt. Among the substances possessing an optical sensitizing power the following are important:—

For the greenish blue—Chrysaniline, acridine yellow, uranine.

For the yellowish green—Eosin, erythrosin, quinoline red.

For the orange -Cyanine, methyl violet.

For the orange red-Nigrosine, pinacyanol.

For the red and infra-red—Dicyanin, Neocyanin, Kryptocyanine

All these substances do not have the same importance. Eosin and erythrosin which show the maximum of absorption in the yellow green part of the spectrum are very convenient for the purpose of sensitization to visible light. Cyanine which absorbs specially in the orange increases the sensitiveness to red light better than eosin, but it has a tendency to fog the plates as it exerts a marked reducing action on the silver halide and hence is seldom used without mixing it with other sensitizers. Most of these sensitizers are basic dyes containing iodine and can act as reducing agents specially in presence of light. Hence they perform dual functions, i.e., marked absorption of visible light which helps in the decomposition of silver halide, and photo-reduction of the silver halide. Both these functions are prominent in the phenomenon of photo-sensitization. The colouring matters of leaves chlorophyll-a $C_{55}H_{72}O_5N_4Mg$., chlorophyll-b $C_{55}H_{70}O_6N_4Mg$., xanthophyll $C_{40}H_{56}O_2$ and carotin $C_{40}H_{56}$, not only absorb visible light markedly but also being reducing agents exert reducing action on the carbonic acid and help in carbohydrate production.

For colour photography by the Lumiere process, it is necessary that the emulsion should possess as uniform a sensitiveness as possible to all parts of the spectrum. Panchromatic plates can be obtained

by sensitizing the ordinary plates with orthochrome-T or ethyl red, both of which possess two maxima of absorption, one in the green and the other in the yellow.

The blue lepidine cyanines extend the sensitivity into the red. Orthochrome-T (p-toluquinaldin-p-toluquinoline ethyl cyanine) gives a very uniform sensitization, whilst pinachrome (p-ethoxy quinaldine p-ethoxy quinoline ethyl cyanine) sensitizes upto 6500°A. pinaverdol (p-toluquinaldine quinoline methyl cyanine) is particularly effective in the green and yellow. True panchromatic sensitivity is obtainable with pinacyanol and ethyl cyanine, both being effective in 6000°A. Dicyanin and neocyanine are useful right upto the extreme limit of visible red and the near infra-red, without causing undue predominance at the other end of the visible spectrum. 'Homocol' and 'Isocol' produced by the Baeyer company are of this type. Kryptocyanin acts as a good sensitizer for the near infra red rays. It is efficacious upto 8500°A. and dicyanin even beyond 9000°A. One of the carbocyanines Xenocyanin gives a maximum sensitivity at 9660°A. and extends upto 13500°A.

Pinaverdol and Orthochrome-T are generally very rapidly decolourised on exposure to light in aqueous solutions or thin films and they are basic dyes. They can be applied to tannined cotton but are mainly used for sensitizing photographic plates towards green light.

The isocyanines are reddish purple dyes but too costly and fugitive to be of value for application to fabrics. They sensitize photographic plates upto the orange. The most even and rapid sensitization is caused by the methyl compounds and this action becomes less pronounced when larger alkyl groups are used as substitute. This shows clearly that light sensitiveness generally decreases with increasing molecular weight. Amongst the isocyanin compounds the most valuable ones are ethyl red, sensitol green or pinaverdol. The carbocyanines sensitize photographic plates in the yellow red parts of the spectrum and are more active than isocyanines. Unlike the corres-

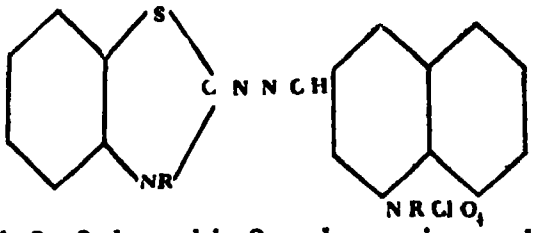
ponding isocyanines, the methyl carbocyanines are poor sensitizers. The ethyl derivatives are the best and the higher alkyl derivatives fall off in value as the series is ascended. This shows again that an increase in the molecular weight makes the dye more stable. The most valuable substance of this class is Pinacyanol or sensitol red which is 1 : 1 diethyl 2 : 2 carbocyanine iodide.

The thiocarbocyanines are bluish red or purple dyes. They can be applied to tannined cotton but are mainly notable for their powerful sensitizing action on the photographic plate. Similarly oxacarbothiocyanines with oxygen in place of sulphur have also been obtained and used as photo-sensitizers.

The indocarbothiocyanines, notably Indolenine red is a pure and coloured dye fast to acid and alkali but only moderately fast to light. In its dyeing properties it resembles Rhodamines. The Apocyanines constitute an exceptional class of substances in which two quinoline nuclei are directly combined. Recently carbocyanine dyes have been prepared with larger polymethine chains containing two heterocyclic nuclei. These include the dicarbocyanine with a connecting chain CH : CH C Br : CH. CH and the tricarbocyanines. The absorption spectra maximum and the production of maximum photographic sensitivity are both nearer to red end of the spectrum than in those of the corresponding simple carbocyanines.

The cyanine dyes including isocyanine, carbocyanine, thiocarbocyanines, indocarbocyanines, oxacarbocyanines, apocyanines have been largely used as photographic sensitizers. The best known amongst them have already been named. All these substances are rich in carbon and hydrogen and do not contain any oxygen but are usually iodo-derivatives. Apparently they behave as reducing agents and are likely to be unstable like iodoform and undergo photo-oxidation by air. Hence they are suitable as sensitizers and act as great absorbents of light and exert reducing action on the silver halide of the photographic plate. Similarly Rose Bengale, eosin, erythrosin also act as photo-sensitizers, for although they contain oxygen, they are rich in carbon and hydrogen and thus exert reducing action on the silver salt.

Aurantia which contains six nitro groups can act as a photographic desensitizer. Being an unstable substance it can undergo decomposition in light and is not reducing in its properties like photosensitizers. The following substance has also been found to be a desensitizer.



3 : 1 Dialkyl 8 : 9 diazothia-2 carbocyanin perchlorate.

The function of the desensitizer appears to be as follows :—

The light energy absorbed by the desensitizer is dissipated as soon as possible without reacting on the silver halide molecule. The desensitizer forms a stable adsorption complex and probably completely covers the silver halide molecule and does not exert any reducing action on the same.

In case of Aurantia, the desensitizing effect may be due to the absorption of light by the molecules and their consequent decomposition, thus the absorbed light is completely dissipated without affecting the photographic emulsion. The action of other desensitizing agents may be explained in the same way. In some cases, however, the light absorbed by the dye is converted into heat immediately. Phenosafranine has been used as a desensitizer for a long time ; it can markedly absorb visible light and is not a reducing agent. Just as a large number of NO_2 groups present in a dye make it unstable, similarly a large number of iodine atoms in a molecule is likely to make a dye also unstable. It seems, therefore, that such iodo compounds after absorbing light can break up and thus dissipate the light energy absorbed and should be able to act as desensitizers. Similarly the perchlorate 3 : 1 dialkyl 8 : 9 diazothia 2 carbocyanin perchlorate may be unstable like Aurantia and may break up by light absorption.

The preparation of cyanin dyes containing nuclei other than the original one, i.e., quinoline, greatly enlarges the field of this group of dyes as did observations that the new type of cyanins had valuable photographic properties. The cyanine dyes of long chains have made possible the preparation of infra-red sensitive photographic materials which are used for long distance photography and also for their power of conferring sensitivity to light of various colours. This has made possible a true rendering of colours in monochrome and led to a great increase in speed, specially to artificial light. The high achievements of modern photography are, in fact, largely due to photographic sensitizers of which cyanines are amongst the most important. Sensitizers have also made possible the technicolour photography

Isocyanines have appeared in the market under the names, ethyl red, Homocol, Isocol, orthochrome-T, pericol, pinachrome, pinachrome violet, pinaverdol and sensitol green; whilst cyanines are marketed under the names of ethyl cyanin-T and quinoline blue.

Fuchs (*Chem. Ztg.* **57**, 1933, 853) pointed out that certain sensitizers containing benzthiozole nuclei are superior to the older cyanines in that, they inhibit chemical fog because they are less reducing in their action on the silver halide. This is also confirmed by Sobolev, Bondareva and Evteeva (*J. Appl. Chem. Russia*, **9**, 1936, 335) who compared the sensitizing action of various substituted cyanines containing benz and naptha-thiozole nuclei. With complex compounds of tungstic or molybdic acid, the indocyanines and indocarbocyanines give coloured lakes which are fast to light.

The I. G. Farben Industries state that indoxyl carbocyanines are specially good photo-sensitizers.

Beattie, Heilbron and Irving (*J. Chem. Soc.* 260, 1932) found that whilst the halogeno-carbocyanines are sensitizers for the deep red or the near infra-red, the corresponding nitro-dicarbocyanines possess desensitizing properties.

The neo cyanines sensitize into the deep infra-red. The azocyanines are dyes with colours varying from yellow to deep red in solution and can act as photographic desensitizers. According to Brooker and

Keys (*J. Franklin Ins.* **210**, 1935, 255) the furthest photographic excursions into the infra-red have been made possible by the discovery of long chain tetra- and penta-carbocyanines. On comparing the cyanine dyes, the paradimethyl aminobenzyl-benzylidin, quinaldine ethi-iodide and paradimethyl amino anil of quinaldialdine aldehyde ethi-iodide on one hand and on the other hand paradimethyl amino-benzaldine-β naphtha quinaldine ethi-iodide and the paradimethyl amino anil of β-naphtha-quinaldine aldeyhyde-ethi-iodide, it is found that the replacement of : CH by : N had the effect of broadening the absorption band, decreasing its intensity and shifting it towards the red. If the linking is by a : CH group, which is reducing in its action, the dye is a photographic sensitizer, but if replaced by a nitrogen atom it possesses desensitizing properties. This appears to be a general rule. It is clear, therefore, that both photographic sensitizers and desensitizers must possess strong light absorption power. But the sensitizer is much more reducing in its action.

It is well known that the ordinary photographic plate is not sensitive to ultra-violet light of radiations shorter than 2200° A. and this has been attributed to the absorption of the incident radiation by gelatine.

Schumann (*Ann. der Physik.* **5**, 1901, 349) showed that plates made with as little gelatine as possible were sensitive to radiations of wavelength 1250 to 2200° A. It is clear, therefore, that in ordinary photographic plates, short ultra-violet light is completely absorbed before it can reach the silver halide. These observations throw considerable light on the functions of photographic desensitizers which like gelatine actually absorb the whole of the incident light before it can reach the silver halide. All desensitizers must be capable of absorbing the incident radiations almost as completely as possible, so that none of the incident radiations can penetrate and affect the silver halide on the photographic plate.

The fogging action of some sensitizers on photographic plate is chiefly due to the reducing action of the sensitizer on the silver halides. All sensitizers which are readily bleached by absorption of oxygen in

presence of light are the ones which generally fog the photographic plates.

In this connection the observations of Padoa and Mervini (*Atti R Acad Lincei* **25,** 1916, 168) showing that the action of hydroquinone in developing photographic plates is not only accelerated at higher temperatures but the silver bromide which has not been affected by light is also reduced and the plate becomes foggy, are of great interest.

It has been already stated that basic dyes are more reducing in properties than acid dyes and are less fast than the acid dyes. Moreover more basic dyes are used as photosensitizers than acid dyes because basic dyes not only absorb light but also reduce the silver halide specially in light These observations are supported by the results obtained by Schmidt (*Z Wiss. Phot.* **26,** 1928, 86) who has reported that with photographic plates sensitized with basic dyes, there is more marked reduction in the sensitivity than with acid dyes, when the plates are treated with potassium chromate and sulphuric acid ; the reason is that the basic dyes absorbed by the silver halide are more readily oxidised by the chromic acid than are the acid dyes which are less reducing in their properties.

The tetra- and penta carbocyanines are excellent photo-sensitizers but are unstable dyes and the stability decreases as the chain is elongated.

Because of the very great importance of cyanine dyes in photosensitization and desensitization numerous complex cyanine dyes including isocyanines, thiacyanines, thiacarbocyanines, symmetrical and unsymmetrical carbocyanines, oxacyanines, oxacarbocyanines, selenacyanines, selena-carbocyanines, thiazolecyanines, thiazole carbocyanines, oxazole cyanines, selana-zolocyanines, thiazolino carbocyanines, neocyanines, apocyanines, azacyanines, etc. have been prepared and their properties studied with great vigour in many countries.

The great increase in speed of panchromatic emulsions witnessed in recent years has been largely due to the new technique of 'super sensitization'. That it is possible to attain sensitization by the addi-

tion of such super sensitizers greater than the sum total of the individual sensitizers, is claimed by C. E. K. Mees. An alcoholic solution of the sensitizer and the super sensitizer is diluted with water and added to the emulsion. As for instance, ten parts of pinacyanol may be super sensitized with one part of pinaflavol, the region of response induced by each overlapping. The net effect is to obtain greater speed in sensitized region than the sum of the two sensitivities conferred by each separately. Another example is that of a thiacarbocyanin, super sensitized by the addition of 8—alkyl diabenz-thiacarbocyanin. It seems that in such cases the light absorption by the mixture is greater than the absorptions of the two sensitizers estimated separately (Compare Dhar and co-workers *J. Indian Chem. Soc.* **11,** 33, 311, 629 (1934), **17,** 673 (1940).

The amount of these sensitizers added to an emulsion is small as compared with fluorescein salts. About 0.05 per cent of the weight of silver bromide would be used in the case of pinacynol; 0.07, per cent in the case of pinachrome, orthochrome-T or pinaverdol. These dyes absorb light very markedly and are all rapidly decolourised on exposure to light in form of aqueous solutions or thin films.

SUMMARY.

1. Basic colouring matters usually contain large number of carbon and hydrogen atoms and behave as weak reducing agents and are oxidised by the oxygen of the air, specially in presence of light and thus become light fugitive.

2. Acidic dyes are richer in oxygen than the basic dyes and are not oxidized by atmospheric oxygen as much as the basic dyes.

3. In general basic dyes have smaller molecular weights than acidic dyes. The greater the molecular weight of a dye, the greater is its stability towards photo-oxidation.

4. The acidic dyes exist when mixed with water mostly either as finely divided particles insoluble in water or colloidal aggregates. The basic dyes usually exist in the molecular condition when dissolved in water.

5. The naturally occurring colouring matters contain more oxygen than the artificial basic dyes and resist photo-oxidation specially when they are in the colloidal condition or protected by other colloids.

6 When fluorescent and non fluorescent colouring matters in alcoholic and aqueous solutions are oxidized by ozone or hydrogen peroxide and ferrous sulphate, a glow is observed The glow is more pronounced with fluorescent colouring substances The bleaching of fluorescent colouring matters is not caused by their fluorescence but is due to their photo oxidation or photo decomposition

7 A colouring matter can fade due to (1) photo-decomposition, (2) photo-oxidation by air, (3) photo reduction by the fibre or the mordant

8 Photo sensitisers play a very important part in modern photography The colouring matters used as photo sensitizer perform dual functions, i e, act as a marked absorbent of visible light and exert reducing action on the silver halide Photo-sensitizers are usually basic dyes

9 Photographic desensitizers are also good absorbents of light but cannot exert reducing action on the silver halide The desensitizing effect is chiefly due to the complete absorption of light by the desensitizing colouring matter Thus the light cannot reach and affect the silver halide In the case of some desensitizers the absorbed light breaks up the desensitizer molecules and is completely dissipated before it reaches the silver halide particles

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART III] SECTION A [VOL. 18

ON THE FLOW OF AIR THROUGH CHINK OF A REED VIBRATOR

By

RAM GOPAL CHATTERJI, M. SC.

[Communicated by Dr. R. N. Ghosh, D. Sc., F. N. I., F.A.S.]
Received on May 13, 1949.

This paper gives a report of the experimental work on the flow of air through chinks in the case of (1) stationary and (2) vibrating reeds. The production of sound waves by the periodic efflux of air through the variable chink of a vibrating reed is a well known phenomenon and has applications as acoustical sources. The present experimental work was undertaken to determine the nature of air flow as it comes out of the chink and the resulting pressure changes in the outer regions of the flow. We have found a zone of negative pressure on the rear side of the reed showing that Kirchoff's law of flow are not obeyed. Similar zones have been observed earlier by Fage and Johansen (1927) in the case of flow behind an inclined flat plate.

We have also studied for the first time the variation of pressure with time near the chink. By taking into account the effect of viscosity on air flow and by a modification of the theory of Ghosh (1946) on maintained vibration, we have been able to account for the phenomena in a general way. There is a good similarity between the experimental and theoretical curves which suggests that viscosity does play an important part in the flow of air.

The experimental work was divided into two parts. In the first part measurements of velocity of flow were taken and in the second pressures at different points were measured. These observations were

taken for both stationary and vibrating reeds. Study of variation of pressure with time has been done by oscillographic method.

To achieve these the outlet end of a wind tunnel was closed with a wooden disc to which was screwed a small wooden box. There was a rectangular slit in the wooden disc to allow wind to enter the box and in order to minimise the streaming motion from the wind tunnel, waste cotton padding was inserted in the proper places. This was done to simulate the condition of the case of harmonium reed vibrator where static pressure is developed with the help of bellows By this device sufficient pressure was developed within the box. The magnitude of the pressure developed in the box was adjusted by the speed of the blower.

The reed vibrator was housed in a slot 1″×4½″ made in a brass plate 1/8″ thick which was screwed to the lid of the box. The reed was arranged to be in flush with that surface of the brass plate which faced the interior of the box and thus chink was formed when the reed moved towards its inward position. In the case of stationary reed observations it was kept slightly inclined to the plane of the slot so that air would issue out through the chink which was formed along the length and the tip of the reed. Observations were taken over the reed at different points in one plane The observations were repeated for planes at different heights.

VELOCITY MEASUREMENTS

For measurements of velocities a hot wire anemometer was used. As the direction of air greatly influences the cooling effect, the anemometer wire was placed in such a manner that the wire was always normal to the wind flow in which position the cooling effect is maximum. This was assured by placing the wire parallel to the longer edge of the reed. Length of the anemometer wire was chosen to be suitably small in order that it may record air flow at a point which may be taken to be the middle point of the wire. Further the leads to the wire were oriented practically parallel to the direction of wind flow in order that they may produce least disturbance at the point of observation. The current through the anemometer wire was adjusted with the help of a series variable resistance such that in the absence of

any air flow, the anemometer wire became red hot. The current was noted. The potential difference E_0 across it, for the wind velocity zero, was measured by a potentiometer. For measuring velocity of air flow 'v' at a point, the anemometer wire was placed in confirmity of above requirements the current through it was adjusted to the above noted value and the potential difference across the wire E_v was recorded. In order to minimise any change in current due to change in the resistance in the hot wire, the variable resistance used in series with it was chosen to be suitably large The instrument was found suitable for measurements of small wind velocities of our experiments. For practical purposes we may take the wind velocity to be given by $v = k\sqrt{E_0 - E_v}$ where k is a constant of proportionality In the case of vibrating reed as the velocity of air is not constant, $k\sqrt{E_0 - E_v}$ gives the r. m s. value of the velocity. Measurements of velocity were taken at different points in a plane of line of flow lying at fixed height above the reed, the least height in the case of vibrating reed being arranged so that the reed did not touch the hot wire

For measurements of average dynamic pressure, a special inclined manometer was constructed It was made out of a glass tubing about 4 mm in diameter, the extended part of the manometer being formed into a glass probe, the end of which was closed and a small hole of the size of 2 mm diameter was made very near to it The tube was placed in such a manner that the flow of wind was tangential to the surface of the hole at the point where measurement of pressure was desired to be taken The manometer orifice was purposely made small and the edges of the hole were smoothened so that no sharp ridge was projected against the flow of air, as any ridge would slacken the velocity with consequent development of stagnant pressure near the orifice In taking pressure readings which are small, parallax error was avoided by placing a second scale about 5 ft. behind the manometer scale.

In the case of vibrating reed, the absolute values of r.m.s. pressures at various points were found out with the help of a calibrated Western Electric 640 AA type microphone and associated amplifier. A small brass probe was used for measurement of pressure at a point; the attenuation due to probe was neglected as the frequency of pressure variation

was small. Figure 4 shows the r.m.s. pressure curve. We find the r.m.s. value comes out to be about 70% of the constant pressure inside the chamber. This is the order of the r.m.s. value predicted from our theoretical consideration (see figure 7) given later.

Observations : -

Plane of observation :—Normal to the plane of the slot in the brass plate and one centimeter from its shorter free end.

x and z are two perpendicular directions in the plane of observation with the edge of the slot as origin, values of x being measured towards the middle of the reed in a direction parallel to shorter free end of the slot

(*A*) *Velocity Observations :—*

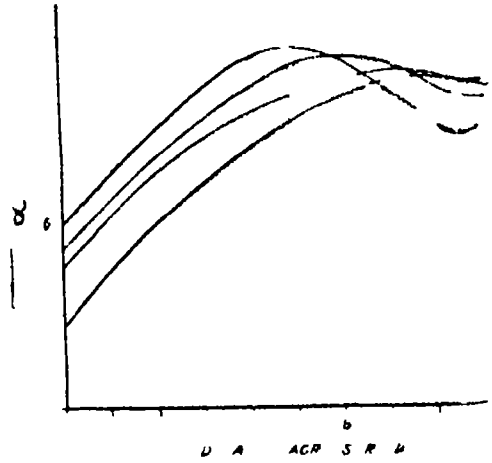
Constant current through anemometer wire = 0·7 amps.

E. M. F. across hot wire (E_0) for zero velocity of air 1·7225 volts.

Vibrating reed.

Distance across the reed 'x' cm.	Height z=3 mm.		Height z=5 mm.		Height z=1 cm		Height z=2 cm	
	E_e	$\sqrt{(E_e-E_0)}$	E_e	$\sqrt{(E_e-E_0)}$	E_e	$\sqrt{(E_e-E_0)}$	E_e	$\sqrt{(E_e-E_0)}$
—·4	1·3716	·593	1·3918	·575	1·4036	565	1·4824	·490
—·2	1·2960	·653	—	—	1 3364	622	1·4250	·546
0	1 2460	690	1 2588	681	1·3041	·647	1·3705	·593
·2	1 1673	·745	1·2194	709	1 2580	681	1 3150	·638
·4	1·1275	·771	1·1717	·742	1 2208	·703	1·2675	·675
·6	1·1120	·782	1 3750	·765	1·1690	·730	1·2707	·707
·8	1·1365	·765	1·1254	·772	1·1607	·749	1·1870	·731
1·0	1 1820	·736	1·1394	·763	1·1540	·754	1·1673	·745
1·2	1·2460	·690	1·1878	·731	1·1670	·745	1·1690	·743
1·4	1·2345	·699	1·1943	·727	1·1730	·740	1·1678	·744

These curves show that the velocity with distance relations have remarkable similarity in the cases of vibrating and stationary reeds



[illegible]

So we may conclude that the stream lin[illegible] fl[illegible] [illegible] in the two cases Further from the graphs we find that the maxim[illegible] velocity curves approaches the centre of the reed asymptotically as we go higher above the plane of the reed

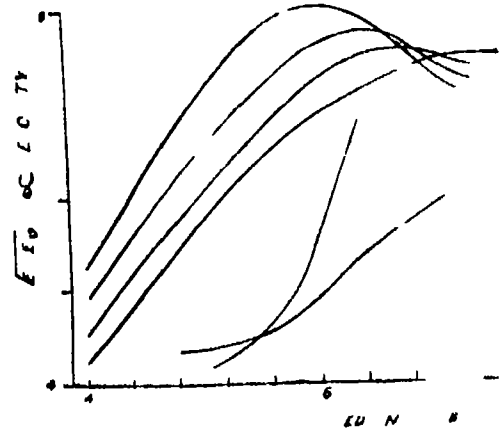


Fig 2

(B *Pressure Observati*

The following tables show the pressure observations which were taken with the help of apparatus described earlier

Stationary Reed

| Di t ce cr ss t e reed x cm | He ghts | | |

The isobars in the cases of stationary and vibrating reeds are similar. We make the following observations from the curves. The curve for normal pressure starts from a height of about 5 mm from

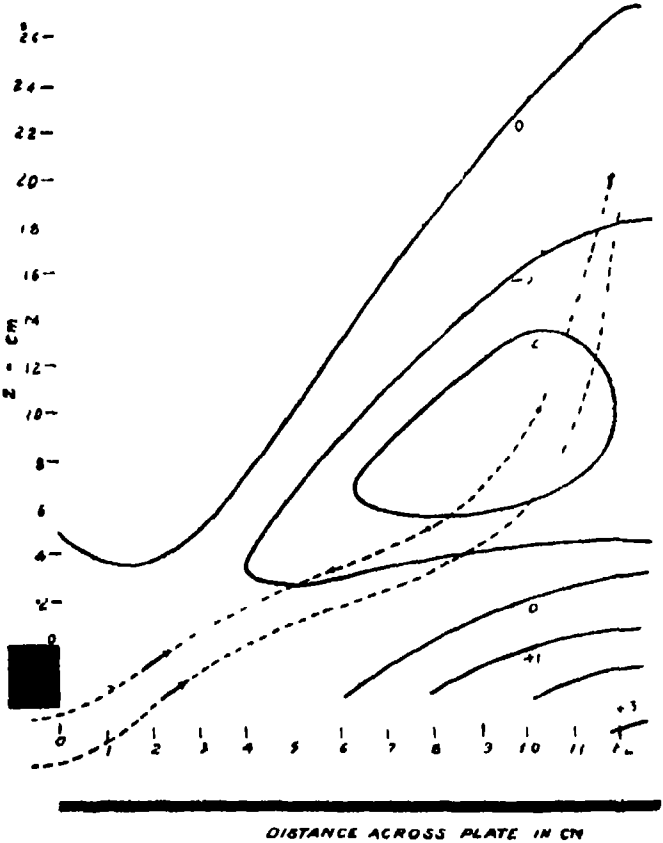


FIG No 3

the upper plane of aperture. It rises very quickly towards the middle of the reed and reaches a height of about 2·7 cm. at the middle of the reed. Lower down of this isobar is the isobar of −·5 mm. which does not continue upto chink but bends round at a distance of 4 mm. across the reed. Practically enclosed by this isobar is the isobar of −1·0 mm which indicates that the zone of maximum negative pressure is at a height of one cm. and at a distance of ·8 cm. across the reed. As we go lower down from this zone of maximum negative pressure, we meet isobars with increasing pressure till finally just at

the back of the middle portion of the reed the pressure is about 3 mm. The zone of negative pressure on the reed has been marked, which

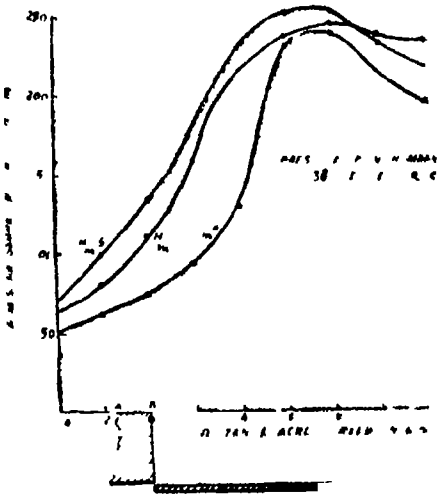


Fig 4

ought not to have been there according to Kirchoffs law. Observations of the pressure very near the mean position of reed in the vibrating case could not be taken due to vibratory motion of the reed, but as we have established that stream lines of flow are similar in the two cases, we conclude from the observations on the stationary reed, that there exists a zone of negative pressure just at the back of the reed near chinks and that the mid region between the chinks is a zone of excess pressure.

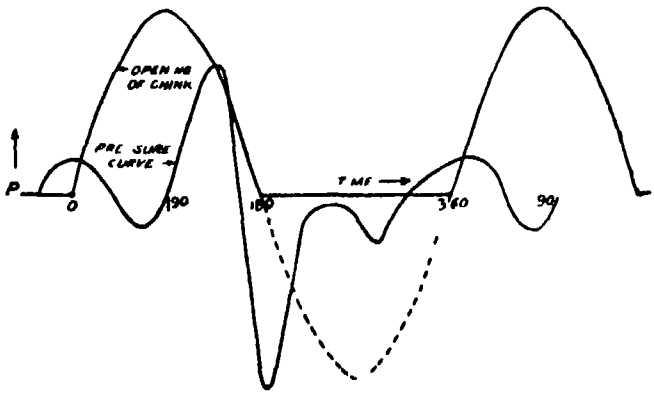
From the nature of isobars, as also from the considerations of points of maximum velocity at given heights we can draw the stream lines as indicated by the dotted lines in the graph for stationary reeds

Phase Relation Between Chink Width And Pressure

It is very important to know in what manner the chink width changes and the pressure in the outside regions follows the changes or lags behind. In order to investigate these questions the pressure changes near the reed were photographed by means of an oscillograph.

In order to determine the phases of maximum and minimum pressure changes with the variations of the chink width due to upward and downward motion of the reed the following device was made.

A bent tube, with orifice as in the case of the probe of manometer, lead the pressure variations into a brass chamber specially designed to enclose a carbon microphone The resulting electrical impulses due to pressure variations were applied through a transformer to the vertical deflecting plates of an oscillograph after amplification, a synchronised sweep frequency being applied to the horizontal deflecting plates. In order to mark the phase of vibration of reed in the resulting pressure-variation pattern a bent wire was fixed in such a manner that the reed in one of its two extreme positions of vibrations just touched the wire and there by short circuited the secondary of transformer. As the microphone voltage applied to oscillograph got short circuited, dots appeared on the pattern at such instances. We should make an allowance of 90° in phase as the secondary voltage is so much out of phase with primary current which is in phase with pressure variation. A photograph for pressure variations at a point 1·5 cm. from the chink and in the plane one centimeter from the



Pressure Variations near Chink.

Fig 5

shortest edge of the seat for reed was taken and a figure showing the associated chink width variations was drawn out of it.

In the case of the figure showing the pressure variations just near the chinks we observe that just as the reed begins to move downwards

i.e., just as the chink begins to open pressure is slightly positive, as the chinks open further the pressure becomes slightly negative. It is slightly positive when the chink is open to its miximum extent. After this instant the reed retraces back towards its mean position and the pressure increases and becomes large. Just before the chink is closed the pressure decreases rapidly and becomes zero. When the reed reaches its mean position the pressure becomes maximum negative. Now as the reed moves upward, the chink is practically closed and negative pressure predominates for a major part of this half cycle. It was observed from the figures* that the average pressure very near the back of the reed is negative in the regions near the chinks and is positive midway between the chinks. The same conclusion was arrived at by manometric observations.

PRESSURE AND CHINK-WIDTH RELATION

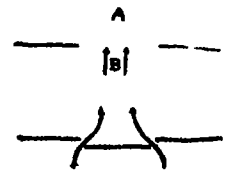
From the nature of the flow pattern and isobars it is apparent that the flow behind the chink is governed largely by viscosity of air and laws of potential flow are departed from We assume that the flow velocity u is given by

$$u = K.\Delta P \xi$$

where, K is conductivity of the chink (dimension LT/M). This will hold true as long as the chink is fine and viscosity is the predominant factor in determining the flow. Hence the volume of air flowing through the chink per second will be given by

$$Q = K.\Delta P.\xi^2 b \qquad (1)$$

where b represents the effective length of the chink. ΔP is the difference of pressure between the zones A and B as shown in the figure. Though in our case the flow is not exactly similar as will be clear from the following diagram but the flow will be dimensionally similar and Q will be given by an expression similar to (1) excepting that the constant K will be different in the two cases.



*Other figures not given in the text.

In the present case since the wave-length is large the air issuing out of the chink will behave like an incompressible fluid in the neighbourhood of the chink and then we can take the above equation to hold true in this case.

In the case of a vibrating reed the chink width will simply be the displacement of the reed from its normal position. Using the formula (Ghosh 1946) for excess pressure 'p' in the outside regions we get.

$$p = \frac{c\rho}{2\pi R^2} \cdot \frac{j\omega Q}{(c/R + j\omega)} \tag{2}$$

Since $\Delta P = P - p$, by combining equations (1) and (2) we get.

$$p = PKb \frac{\xi^2}{Kb\xi^2 - j\dfrac{2\pi R}{\omega\rho} + \dfrac{2\pi K^2}{\rho}} \tag{3}$$

Where P represents the constant excess of pressure within the chamber. ξ will be given by

$$\xi = \xi_0 e^{j\omega t} \tag{4}$$

The real part of which represents the displacement of the reed, viz.

$$\xi = \xi_0 \cos \omega t \tag{5}$$

Substituting the exponential value of ξ in equation (3) we get

$$p = P \frac{\xi^2_0(\cos 2\omega t + j \sin 2\omega t)}{\xi^2_0(\cos 2\omega t + j \sin 2\omega t) - j\dfrac{1}{Kb} \cdot \dfrac{R}{f\rho} + \dfrac{2\pi}{c\rho} \cdot R^2 \cdot \dfrac{1}{Kb}} \tag{6}$$

In our case, $R = 1.5$ *cm*, $f = 46$ *cycles/sec*, $b = 5.8$ *cm.*, $\xi = 0{\cdot}7$ *cm.*

Taking the following values for the constants, $K = 5$ *cm. sec*, gm^{-1}., $\rho = 1.25 \times 10^{-3}$ *gm/c c*, $\rho c = 42$,

The amplitude of 'p' for various values of 'pt' has been calculated from the equation (6) and the curve plotted as in below. By comparing this diagram with that obtained by oscillographic record we observe that the two curves are similar except for a change of phase. We expect some change of phase to occur because of some finite inductance in the primary of the transformer used in the microphone

circuit. We find the negative amplitude of pressure to be larger in both the cases. The similarity between the experimental curve

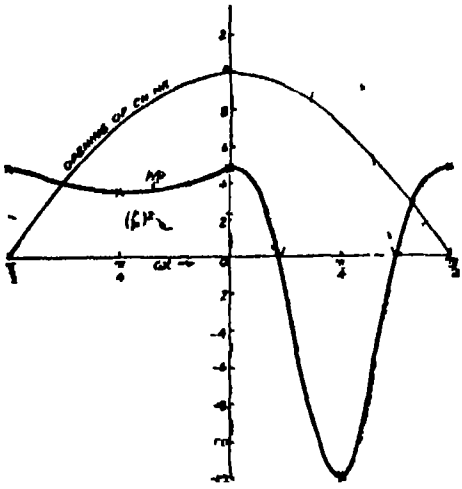


Fig 7

and the curve predicted by the law of slow motion under viscosity shows that viscosity plays an important part in the flow of air through chink of a reed vibrator. The vibrating reed practically closes down the chink for one half of its period of vibration and consequently this part of flow has not been dealt with.

Fig. 6, shows also the plot of the square of theoretical pressure for the interval the reed opens. From this by measurement of area in Fig. 7, we find that the r m.s. value of pressure at the point under consideration is about 70% of the pressure P inside the chamber as was observed experimentally.

Velocity Curves

At large distances from the aperture it has been found (Roscoe 1949) that the radial velocity U at a distance r is given by

$$U = \frac{2A\zeta^2}{r^4} \tag{7}$$

where ζ is the perpendicular distance from the plane of aperture. The two curves plotted in the velocity diagram (Fig. 2) are those calculated out from equation (7). Although the condition required by the equation are not fully realised but there is similarity between the two

curves. It has been possible to make quantitative measurements and thus to verify the theory developed.

Conclusion

The paper gives an account of measurement of 'flow' through chinks of (1) constant width and (2) the same in the case of chink of periodically varying width. The types of flow in both cases have been found to be similar. The flow is least near the chink and increases as the point of observation is moved along one plane towards the dead centre; definitely there is a region of maximum flow before reaching the dead region. If the plane of observation is raised higher the same type follows but the maximum shifts towards left (Fig 1 and 2). The pressure measurement were done with a manometric probe; the isobars are shown in figure (3) in the case of a chink of fixed width. The measurements in the case of a chink of variable width gave a mean value which was not found to be accurate but the type of isobars was practically similar.

It has been found that the flow is governed by viscosity and the law formulated by Roscoe seems to hold true in the case of chink described in the text. The volume rate of flow is proportional to difference of pressure and to the square of the chink width in the case where the length is large in comparision to the width. A comparision of the pressure time curve with the oscillographic record shows remarkable similarity in the case of a chink of periodically varying width. The theory developed has been quantitatively verified experimentally.

Acknowledgement:—

My sincerest thanks are due to Prof. R. N. Ghosh, D. Sc., F N. I., F. A. S. (America) for his keen interest in the progress of the work and his able guidance; and the Vice-Chancellor of the Allahabad University, for meeting the cost of the paper in the Proceedings of the National Academy of Sciences, India, Allahabad.

References

Fage and Johansen *Proc. Roy. Soc.*, ... 1927, 116, 170.
R. N. Ghosh *Proc. Nat. Ins. Sci Ind.* ... ... 1946, 12, 208.
Roscoe *Phil. Mag.* ... ... 1949, 40, 344.

A QUALITATIVE STUDY OF FLAME TEST FOR TIN, GOLD AND BISMUTH

By

R. C. MEHROTRA

(CHEMICAL LABORATORIES, THE UNIVERSITY OF ALLAHABAD, ALLAHABAD.)

(Received on 4-3-1949)

A blue mantle test for tin has been described by H. Meissner[1] as follows: 'The substance or solution is treated in a porcelain dish with an excess of hydrochloric acid and a piece of pure zinc rod is added The mixture is well stirred by means of a test tube filled with cold water and the tube is then inserted into a non-luminous flame. A blue mantle around the moistened part of the tube indicates the presence of tin.' F. L. Hahn[2] tried to find out the cause of the above test and came to the conclusion that probably the blue luminiscence is not due to the formation of stannic hydride as was assumed by Meissner. E. Schroer and A. Balandin[3] find that the blue luminiscence cannot be due to the excitation by free electrons. J. Hoffmann[4] applied the test to glass analysis and again describes the test to appear by the reduction of glass by zinc and hydrochloric acid which affords SnH_4 and this SnH_4 deposits on the cold surface of the tube and colours the flame blue.

The test in all probability is not due to the formation of tin hydrides. It was observed by Salet[5] and later confirmed by Bancroft and Weiser[6] that the tin chlorides themselves colour the Bunsen flame blue, the tin bromides colour it green and the iodide imparts a yellow colour to the flame. Therefore, the test for tin was repeated in the manner described by Meissner and it was found that if stannous or stannic chloride itself is dissolved in water and a test tube full of water placed in the solution, then when the test tube is brought to

the Bunsen burner, a blue mantle surrounds the bottom of the test tube. The only perceptible effect of addition of zinc and hydrochloric acid is to increase the intensity of the blue luminiscence. If the tin chloride is replaced by tin bromide or iodide, the colour of the mantle was respectively green and yellow. However, when the test is repeated with zinc and sulphuric acid in the place of hydrochloric acid, no blue mantle appears at all. It was found that the presence of sulphate, nitrate or fluoride ions inhibits the test, when their alkali salts are added in sufficient quantity to a mixture of tin salt, zinc and hydrochloric acid. The appearance of the blue mantle with tin salts alone makes the hydride theory very improbable. It might be argued that the free hydrogen present in the gas supplied to the Bunsen burner might be playing a part, but the instability of the tin hydride as prepared by Paneth and Furth[7] by the action of metallic magnesium on a solution of tin chloride or sulphate in hydrochloric acid rules out the above line of argument. Moreover, the non-appearance of the test when hydrochloric acid is replaced by sulphuric acid cannot be explained by the hydride theory. As was shown by Schroer and Balandin[8] who suggested that the method may be used for halogen acid, the reaction is a test of the chloride, bromide and iodide ions rather than that of tin. The chloride and bromide ions, somehow exhibit the test in the presence of tin ions. It occurred to the author that it may be a case of chemiluminiscence brought about by the recombination of halogen atoms formed from the dissociation of the tin salt according to the following scheme :

$$\mathrm{Sn\,Cl_4} \rightleftharpoons \mathrm{Sn\,Cl_3} + \mathrm{Cl}$$

$$\Downarrow\uparrow$$

$$\mathrm{Sn\,Cl_3} + \mathrm{Cl}$$

$$\mathrm{Cl} + \mathrm{Cl} \rightleftharpoons \mathrm{Cl_2} + h\nu \text{ (luminiscence)}$$

$$\mathrm{Sn\,Cl_2} + \mathrm{O} \text{ (from atmosphere)} \rightarrow \mathrm{Sn\,O\,Cl_2}$$

$$\mathrm{Sn\,O\,Cl_2} \rightleftharpoons \mathrm{Sn\,O\,Cl} + \mathrm{Cl}$$

$$\Downarrow\uparrow$$

$$\mathrm{Sn\,O} + \mathrm{Cl}$$

Similarly, $\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2} + h\nu$ (luminiscence)

The order of the luminiscence observed may be taken from the convergence limit of chlorine and bromine in their predissociation spectra. The convergence limits of chlorine and bromine are at 4785° and 5107° A, which lie in the blue and green region respectively. The heats of dissociation of chlorine and bromine are 57000 and 46200 calories respectively and so the wave-length of the light emitted on the recombination of the atoms would be 4987° and 6147° A respectively (from $Q=h\nu=hc/\lambda$).

If the above mechanism about the test were correct, similar colours must be observed from the chlorides and bromides of all metals where tendency to similar thermal dissociation exists. On applying this test, it was found that mercuric, thallium, platinum, manganese, cobalt, lead, nickel, cadmium and arsenic salts do not show any similar coloration. However, it was found that bismuth and gold salts do show similar tests. The purpose of the present communication is primarily to describe the flame test for gold which is of practical importance, and to describe the similar coloration of the luminiscence that is shown by bismuth and gold salts so that it may not be confused for the blue luminiscence shown by tin salts in the Meissner's test. It further describes the interfering factors in the presence of which the flame test for tin is suppressed.

Flame reactions of tin salts :

Stannic and stannous chloride gave a very brilliant blue mantle, which increased in intensity on the addition of hydrochloric acid. Action of zinc further does not appear to have much influence. The blue luminiscence is suppressed if the hydrochloric acid is replaced by sulphuric acid and the test does not appear even when zinc is added in the presence of sulphuric acid. The blue luminiscence is also suppressed by the addition of ammonium sulphate, nitrate or fluoride to the tin salt. In the presence of hydrochloric acid, larger quantity of sulphate, nitrate or fluoride ions is necessary to suppress the test than without it.

Stannic bromide gave a brilliant green mantle which increased in its intensity with the addition of hydrobromic acid. If hydrochloric acid is added in the place of hydrobromic acid, the green mantle characteristic of the bromide is replaced by the blue mantle characteristic of the chloride. If the amount of hydrochloric acid is small or the solution to be tested contains some other source of the bromide ions, so that the amount of bromide ions present is comparable with the amount of the hydrochloric acid added, then the green luminiscence also appears when the blue luminiscence has faded away.

Stannic iodide gave a greenish yellow mantle and showed a behaviour similar to that of the bromide with hydrochloric acid.

Tin sulphate and nitrate did not show any blue luminiscence either when alone or in the presence of sulphuric acid and zinc. The luminiscence appeared on the addition of concentrated hydrochloric acid, but was again suppressed when sulphate or nitrate ions are added in considerable amounts.

Flame reactions of bismuth salts :

As the chloride, bromide and iodide of bismuth were not obtainable in pure form, a pure Kahlbaum sample of Bismuth carbonate (tested to be free from tin) was taken and the flame test applied in a manner similar to the Meissner test for tin .

Bismuth carbonate with hydrochloric acid gives a greenish blue mantle. Addition of zinc begins to precipitate metallic bismuth and does not improve the intensity of the mantle. However, the test remains positive so long as all the bismuth ions have not been removed from the solution. Addition of tin salt, however, replaces the greenish blue mantle of bismuth chloride by the intense blue luminiscence characteristic of tin chloride.

Bismuth carbonate and hydrobromic acid gives a yellowish green mantle.

Bismuth carbonate and hydroiodic acid gives a very insensitive reddish mantle.

Bismuth carbonate with sulphuric acid and nitric acid does not give any perceptible mantle at all. Addition of small amounts of hydrochloric acid also in the presence of either of these acids does not make the mantle appear.

Flame reactions of gold salts:

On applying the flame test to gold chloride in a manner similar to that described by Meissner for tin, a gold chloride solution in the presence of hydrochloric acid gave a brilliant green mantle. The gold chloride solution itself gives the mantle and along with the appearance of the green luminiscence, a film of brightly shining metallic gold is deposited on the bottom of the test tube. The mantle becomes much more intense in the presence of considerable concentrated hydrochloric acid. Addition of a speck of metallic zinc improves it slightly. The test, like the similar test of the bismuth and tin chlorides is suppressed by the presence of a considerable amount of sulphuric or nitric acid.

Gold chloride solution in the presence of hydrobromic acid gives a pale orange mantle which is not improved much in its intensity even on the addition of metallic zinc.

Gold chloride solution in the presence of hydroiodic acid does not give any mantle. This is probably due to the decomposition of the auric iodide with the simultaneous deposition of iodine.

On the basis of the above reactions, a green mantle test for gold has been recently described[9]. To perform the test, the gold salt solution is taken in a beaker, concentrated hydrochloric acid added to it and a small speck of zinc is put in. A test tube full of water is held at the point where hydrogen is evolving out briskly and then the test tube is taken to the hottest part of the Bunsen flame. If gold

is present in the solution being tested, a very brilliant green mantle will surround the bottom of the test tube spreading upwards along the sides of the tube. The test is sensitive to 0·1 mgm. of gold per ml. of the concentrated hydrochloric acid. The test is not interfered by the presence of mercury, lead, silver and platinum ions and so gold is easily detected in an ore or alloy by dissolving the nitric acid insoluble portion in a little aqua regia, evaporating almost to dryness to drive out the nitic acid and then applying the above test. The presence of tin however interferes, replacing the green mantle by the blue mantle characteristic of tin. Copper ions also interfere

The mechanism of the above flame reactions:

Much more quantitative and spectroscopic work is essential, before any definite conclusions as to the cause of the above tests can be reached. Though the purpose of the present communication is mainly practical, it may be mentioned that the scheme suggested above drives support from the similarity in the colours of the mantles from tin, bismuth and gold chlorides. It is of interest to mention here a similar though an observation unnoticed by workers in this field, of M. Polanyi and G. Schay[10], who studied the chemiluminiscence between the alkali metal vapours and tin halides. They observed that highly diluted flames of alkali metals burning in stannic chloride, bromide and iodide emit intense luminiscent and continuous bands. The bands extend from 400 to 550μμ with K and $SnCl_4$, 405 to 540μμ with Na and Sn Cl_4, from 440 to 600μμ with Na and $SnBr_4$, and from 500 to 620μμ with Na and SnI_4. The intensity of the bands is the greatest in the centre of the band and decreases on either side. It is clear that with the naked eye the luminiscences would appear to be respectively blue, green and yellow in the cases of the chloride, bromide and iodide. The chemiluminiscence is explained by a mechanism shown below:

$$Sn X_4 = Sn X_3 + X$$
$$2\ Sn X_3 = Sn X_2 + Sn X_4$$

The mechanism is similar to the one suggested above. However, the suggested mechanism also explains the part played by the cool surface of the test tube or hydrogen gas in providing centres of collision for the halogen atoms to unite, for as shown by Jost[11], the recombination of halogen atoms to form the undissosciated molecule can occur only as a three body process in the gaseous phase or on the walls of the nearby solid surfaces.

However as stated above, much more quantitative work is needed before the mechanism can be definitely established.

Summary

1. The blue mantle test for tin has been studied and it has been found that the colour of the mantle differs with the halide taken. It has been further found that the test is interfered by the presnece of sulphate, nitrate and fluoride ions.

2. Reactions similar to the above have been found to be shown by the halides of bismuth and gold and hence precaution is necessary not to mistake a mantle given by them for the presence of tin.

3. A new sensitive flame test for gold has been described.

4. It has been shown that the blue mantle given by tin cannot be due to the stannic hydride as was supposed. A tentative mechanism has been suggested for the above flame reactions of tin, bismuth and gold.

References

1. H. Meissner, *Z. anal. Chem.*, 80, 247, 1930.
2. F. L. Hahn, *ibid.*, 82, 113, 1930
3. E. Schroer and A. Balandin, *Z. anorg. Chem.*, 189, 258, 1930.
4. J. Hoffmann, *Sprechsaal*, 65, 82, 1932
5. Salet, *Ann. Chim. phys.*, (4) 28, 5, 1873.
6. Bancroft and Weiser, *J. Phy. Chem*, 18, 281, 1914.
7. Paneth and Furth, *Ber.*, 52, 2020, 1919.
8. Schrer and Balandin, *loc. cit.*
9. Mehrotra Nature, 161, 321, 1948.
10. Polanyi and Schay, *Z. Physik*, 47, 814, 1928.
11. Jost, *Z. Phy. Chem.*, 83, 95, 1929.

THE NATURE OF HYDRATED COPPER HYDROXIDE PRECIPITATED AND AGED UNDER DIFFERENT CONDITIONS

By

R. C. MEHROTRA AND S. GHOSH

Chemical Laboratories, The University of Allahabad, Allahabad.

Received on 3-3-49

It is a well known observation that if a solution of caustic alkali be added to a solution of copper salt, the colour of the precipitated hydroxide changes from blue to black just when a drop of the alkali is added in excess. The colour change is generally assumed to involve the conversion of the blue hydrated copper hydroxide to the black cupric oxide. Evidently, the mechanism of the above conversion brought about by a drop of the alkali does not appear to be easily explainable as a simple dehydration process, involving molecular splitting off of water molecules as shown by the following equation:

$$Cu\,(OH)_2 . x\,H_2O \rightleftharpoons CuO + (x+1)\,H_2O \quad . \quad . \quad . \quad . \quad (1)$$

A number of observations recorded below definitely demonstrate that the conversion of hydrated cupric oxide from blue to black variety is not a simple dehydration process. At the same time, it has been shown that the blue precipitate obtained by a deficient amount of the alkali differs in a number of properties from the black precipitate obtained by a slight excess of the alkali. Studies have also been made on the changes exhibited by the hydrated oxide on ageing.

Copper hydroxide was precipitated by the addition of 100. 0c. c. of carefully standardised 0. 2N caustic soda solution to 50. 0c. c. of a 0. 2N copper sulphate solution. As the alkali was slowly added to the copper sulphate solution, the colour of the solution went on becoming lighter and lighter, until about half the amount (50c. c.) of

the alkali had been added, after which the colour began to deepen in shade until deep blue copper hydroxide was precipitated down. The copper hydroxide was filtered off and carefully washed free from sulphate ions. It was observed that althogh just equivalent amount of the alkali had been used, the wash liquor had a little alkaline reaction detectable by the development of pink colour with phenolphthalein. A similar observation[1] had been made by Tommassi and also by Dey and Ghosh that a solution of sodium chloride and sulphate show an alkaline reaction after shaking with hydrous cupric oxide and it is due to preferential adsorption of the anion. The precipitate was washed free from sulphate ions and was divided into five portions as below:

(1) First portion was placed in 100 c.c. of distilled water.

(2) Second portion was placed in 100 c.c. of N/100 caustic soda solution,

(3) Third portion was placed in 100 c.c. of N/10 caustic soda solution,

(4) Fourth one was dried between filter papers and allowed to remain in air,

(5) Fifth portion was carefully dried by filer papers and placed in a desiccator over concentrated sulphuric acid.

The colour changes of the five portions were observed for about a week. The last one in the desiccator remained definitely deep blue whereas the one in contact with atmosphere remaind bluish though at a number of isolated point it turned brown or grey. The first one in distilled water gradually took up a light grey or brownish shade, the second one became almost definitely black, whereas the third one was deep grey, deeper than the first but lighter than the second. The distilled water in portion (1) was tested after a week and found to be neutral even then.

The above colour changes definitely show that the conversion of hydrated cupric oxide from blue to black variety is not a simple

dehydration process represented by the equation (1). If the said equation had represented the real process, then the rate of dehydration would have been slower in presence of water than in the dry atmosphere of the desiccator, while as recorded above, actual experimental observations show just the opposite. However, all the above observations can be easily explained by an extension of Kohlschutter and Tuscher's views[2] regarding the blackening of blue copper hydroxide. According to them, the blackening is not due to a molecular splitting off of water, but due to internal neutralisation as a result of amphoteric dissosciation of copper hydroxide. Their views can be explained by the following equations:

$$Cu\,(OH)_2 = [Cu\,(OH)]^+ + (OH)^- \quad . \; . \; . \quad (2)$$

$$Cu\,(OH)_2 = [H\,Cu\,O_2]^- + H^+ \quad . \; . \; . \quad (3)$$

$$H^+ + (OH)^- = H_2O \quad . \; . \; . \quad (4)$$

$$[Cu(OH)]^+ + [H\,Cu\,O_2]^- = \underset{\underset{2\,Cu\,O}{\|}}{[Cu\,Cu\,O_2]} + H_2O \quad . \; . \; . \quad (5)$$

Thus the process is not a simple dehydration process, but involves internal neutralisation of the acidic and basic forms of cupric hydroxide. The blackening cannot occur in the desiccator, where the dissosciation into the two forms is not possible, but it can occur in presence of water. The immediate blackening by a drop of the alkali can be easily explained on the above views. Moreover, an extension of the above views can also explain why the blackening, as observed above, is maximum in the presence of $N/100$ alkali and then again is lesser in $N/10$ alkali.

The rate of the process (5) will be proportional to $[(Cu\,OH)^+] \times [(H\,Cu\,O_2)^-]$. It can be easily shown that if $a+b$ is constant, then $a \times b$ has a maximum value when $a = b$. Hence the rate of the above process of blackening shall be the greatest at the point where $[Cu\,(OH)^+] = [(H\,Cu\,O_2)^-]$ or at a pH at which the concentration of the two ions due to acidic and basic dissosciation of copper hydroxide are

just equal. The point may be defined as the isoelectric point and can be calculated from the following relationships.

$$\frac{[Cu\ (OH)]^{+}\ [OH]^{-}}{[Cu\ (OH)_2]} = Kb \text{ (Basic dissosciation constant).}$$

$$\frac{[H]^{+}[H\ Cu\ O_2]^{-}}{[Cu\ (OH)_2]} = Ka \text{ (Acidic dissosciation constant)}$$

$$\text{Hence } \frac{[Cu\ OH]^{+}[OH]^{-}}{[H]^{+}[H\ Cu\ O_2]^{-}} = \frac{Kb}{Ka}$$

Now, at the point where $[Cu\ (OH)]^{+} = [H\ Cu\ O_2]^{-}$,

$$\frac{[OH]^{-}}{[H]^{+}} = \frac{Kb}{Ka}$$

$$\text{or } \frac{[OH]^{-2}}{Kw} = \frac{Kb}{Ka}$$

$$\therefore [OH]^{-} = \sqrt{\frac{Kb\,Kw}{Ka}}$$

Hence, the blackening will be maximum when the hydroxyl ion concentration is equal to $\sqrt{\frac{Kb}{Ka} \cdot Kw}$. As is well known, the basic nature of copper hydroxide represented by Kb is much more pronounced than the acidic nature (represented by Ka). Therefore, the isoelectric point will occur in the alkaline range. Now, if the hydroxyl ion concentration be lesser than this value, the basic form $[Cu\ (OH)]^{+}$, due to the ionisation shown by the equation (2), will predominate, whereas if the hydroxyl ion concentration be greater than at the isoelectric point, then the acid form $[H\ Cu\ O_2]^{-}$ arising out of the ionisation shown the equation (3) will be more prominent and hence, in both the c ses, the rate of blackening will be slower than that at the isoelectric point The above discussion explains so simply why the blackening was greatest at a caustic soda concentration of N/100 and was lesser in hydroxyl ion concentration both above and below this value. An effort was made to determine the exact isoelectric point by making acidic buffers of acitic acid sodium acetate mixtures and alkaline buffers of boric acid—borax mixtures. However, it was observed that the borate ions stabilise the blue form due to the ten-

dency of complex formation, hence exact comparisitions could not be made and the exact point could not be determined.

However, the applicability of the theory can be demonstrated by the simple manner in which the observations of a number of previous workers can be easily explained. Tommassi[3] observed that a small concentration of manganous sulphate is able to stabilise the blue colour of copper hydroxide We have observed that this stabilisation is almost permanent. A sample of the precipitate immersed in a dilute (1 %) solution of manganous sulphate placed on 20th September, 1944 has preserved its original greenish blue shade even after the passage of more than four years However, we have observed that the stabilisation is not restricted to manganous sulphate, but a number of salts like manganous chloride, zinc suphate, aluminium sulphate and even copper sulphate itself show the phenomenon. A number of conflicting explanations[4, 5, 6, 7, 8] have been offered within recent years. Bancroft[4] explains the stabilisation to be due to the protective action of adsorbed hydrous oxide of manganese. On Bancroft's views, Weiser[6] finds it unable to explain the mechanism of stabilisation shown by copper sulphate itself and he supposes the stabilisation to be a physical process depending merely on the size of the particles. Fowles[8] tried to explain the stability to be due to the removal of the adsorbed alkali which by its presence would have catalysed the blackening. Kruger[7] point out that only those substances generally exhibited this stabilisations, which by their hydrolysis give an acidic solution. Fowle's[8] explanation is very close to ours, which is evident from the discussion given above, that in the acidic medium the blackening will not occur due to the preponderance of the basic form of the copper hydroxide.

Apart from the above variation in the physical characteristics of the copper hydroxide precipitated and aged under different conditions, we have recently observed[9] that the copper hydroxide precipitated with a slight deficient amount of the alkali differs from the one precipitated with a slight excess of the alkali in its dissolubility in dilute ammonia solutions. In this communication, we want to record a

number of qualitative observations made regarding the variation of the properties of the hydroxide precipitated under different conditions and also the variation in the properties of similarly precipitated hydroxide aged under different conditions:

(1) 51.0c c. of 0.2N caustic soda solution added to 50. 0c. c. of 0. 1M $CuSO_4$ solution

(2) 50 0c. c. of 0 2N caustic soda solution added to 50. 0c. c. of 0. 1M $CuSO_4$ solution.

(3) 50. 0c. c. of 0.2N caustic soda solution added to 51. 0c. c. of 0. 1M $CuSO_4$ solution.

The precipitates were well washed free from all soluble electrolytes and then allowed to age under the following conditions : precipitates obtained (1), (2) and (3) were each divided into three portions and allowed to stand in contact with the following media·

(a) 100 c. c. of distilled water+2c. c. of 0.2N caustic soda.

(b) 100 c. c. of distilled water,

(c) 100 c. c. of distilled water+2c. c. of 0.2N acetic acid.

A comparison of the three samples 1 (b), 2(b) and 3(b) aged under distilled water showed that although all the three had become greyish in shade, the first one was almost black, the second one was a little lighter greyish black in shade, while the third one was still lighter in colour. All the samples aged in alkaline solution became almost equally dark grey in a few days time; all the precipitates aged under acidic media retained their blue colour even after six months of ageing.

Now, the solubility of the above samples, after being aged for about ten days, was tested in a solution of Roschelle salt (sodium potassium tartrate) of the same concentration and also in a dilute solution of ammonia. Judged from the colour of the solution, the alkali aged sample (2a) showed much lesser solubility than the acid aged sample (2c) whereas the solubility of the sample (2b) was midway between those of (2a) and (2c) in both sodium potassium tartrate and ammonia solutions. Similarly, a comparison betwen the water aged samp'es (1b), (2b) and (3b) showed similar relationships. The sample (3b) obtained with a slight excess of copper salt showed the maximum solubility,

whereas the sample (1b) showed the minimum solubility of the three samples.

The above variation in the properties and particularly, the similarity in the range of the solubility exhibited in a basic solvent like ammonia and an acidic solvent like sodium potassium tartrate may appear at the first sight a little difficult to explain. However, they can be easily explained by Bronsted's[10], Lowry's[11], or Lewis [12],[13] views about the nature of acidic and basic substances

According to Bronsted's and Lowry's conceptions of acid and base, both the ammonia (NH_3) molecule and the tartrate ion are basic in nature, because both of them have a tendency to accept protons. Therefore a similarity in the range of the solubility in the two media can be expected. Moreover, the nature of the dissolving substance being basic, that sort of the precipitate will have the highest tendency to dissolve, which has the portion active in this dissolution in the most acidic form. Cu^{++} and $(CuOH)^{+}$ ion can be regarded acidic in nature, because they have a tendency to combine with the basic $(OH)^{-}$ion, as shown by the equations (6) and (7):

$$Cu\,(OH)_2 - \left[Cu\,(OH)\right]^{+} + \left[OH\right]^{-} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

$$\left[Cu\,(OH)\right]^{+} = Cu^{++} + \left[OH\right]^{-} \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

Now from the law of mass action, the concentration of these acidic ions, Cu^{++} and $CuOH^{+}$ will decrease as the concentration of the hydroxyl ions is increased; and therefore with the increasing hydroxyl ion concentration, the solubility in the basic solvents like ammonia and the tartrate ion can be expected to decrease.

According to Lewis' conception, "the acidic and basic nature of a substance is governed by its tendency to accept or donate electron pairs to form covalent bonds, irrespective of whether the transfer of protons is involved or not". Now, the solubiltty of copper hydroxide in both ammonia as well as the tartrate ions is due to the tendency of copper ions to accept the electron pairs donated by the ammonia molecules

or the tartrate ions with the formation of covalent bonds. Hence, the similarity in the dissolution power of ammonia and the tartrate ions, arising out of the same tendency can be easily understood. Moreover, the above mechanism explains the part played by the surface effects due to the precipitation and ageing of the precipitates under different conditions. The precipitate obtained with an excess of alkali or aged under alkaline solutions will develop a negative charge on the particles due to a preferential adsorption of the hydroxyl ions and this charge will go on decreasing or rather may even change its sign when the precipitation or the ageing is carried out in acidic media. Hence, the particles of the precipitate aged under alkaline media, by virtue of the negative charge on them, will retard the electropositive character of the copper ions to accept electron pairs from either ammonia molecules or the tartrate ions and hence the alkali aged precipitate or the precipitate obtained with a slight excess of the alkali will show a much lesser solubility in ammonia or Roschelle salt than the one aged in acidic media or precipitated with a deficient amount of the alkali.

SUMMARY

1. The rate of blackening of hydrated copper hydroxide has been studied under different conditions.

2. It has been shown that the observations on the rates of blackening can be explained by Kohlschutter and Tuscher's views based on internal neutralisation.

3. The theory of iso-electric point has been developed to explain a greater rate of blackening in the presence of N/100 caustic soda than in the presence of N/10 alkali.

4. The phenomenon of the stabilisation of the blue colour of the hydrated copper hydroxide by manganous sulphate, copper sulphate, zinc sulphate etc. has been explained on the above theory.

5. The variation in the nature of the precipitate obtained and aged under different conditions has been studied.

6. The above variation has been explained by Bronsted's and Lowry's definition of acids and bases and also by G. N. Lewis' "Electronic conception of acids and bases."

Reference

1. Tommassi, *Bull. Soc. Chim*, (2), 37, 197, (1882).
2. Kohlschutter and Tuscher: Z. *anorg. Chem.*, 111, 193, (1920).
3. Tommassi: *Compt. Rend.*, 99, 38, (1884).
4. Bancroft: *Z. Phy. Chem.*, 18, 118, (1914).
5. Blucher and Famau: *ibid.*, 18, 629, (1914).
6. Weiser, *ibid.*, 27, 431, (1923).
7. Kruger: *J. Prakt. Chem.*, 108, 278, (1924).
8. Fowles: *Chem. News*, 128, 5, (1925).
9. Mehrotra and Ghosh: *Proc. Nat. Acad. Sci.*, 15, 161, (1946).
10. Bronsted: *Rec. Trav Chim.*, 42, 718, (1923).
11. Lowry: *Chem. and Ind.*, 42, 43, (1923).
12. G. N. Lewis: *J. Frank. Inst.*, 229, 293, (1938).
13. Luder: *Chem. Rev.*, 27, 547, (1940).

PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF COMPLEX STANNIOXALATES

PART II SPECTROSCOPIC STUDY OF $SnCl_4$-$H_2C_2O_4$ SYSTEM

By

ARUN K. DEY AND A. K. BHATTACHARYA

Department of Chemistry, University of Saugar

(Read on 30th April 1949)

ABSTRACT

Ultra violet absorption spectra of mixtures of stannic chloride and oxalic acid solutions have been studied. From an examination of the photographs of the spectra, it has been concluded that the compounds formed have the compositions: $Sn(C_2O_4)_2$ and $H_4Sn(C_2O_4)_4$.

In a number of publications we have inferred that stannic tin forms complex compounds with oxalates, malonates and succinates (1, 2) and also with tartrates (3). In the previous part of the present series (4) we have studied the compositions of the complex compounds formed between tetravalent tin and soluble oxalates by the electrical conductivity method. It has already been pointed out by us (5) that since isolation and subsequent chemical analysis fail to convey a true picture of the complex compounds formed, as the products include double salts and adsorption complexes as well, physico-chemical methods must be adopted to elucidate the compositions of complex ions. In persuance to above the absorption spectra of solutions containing the complex stannioxalate ions have now been studied in the ultra violet region and the results interpreted for the determination of the composition of complex ions. This paper records our results on the study of mixtures of stannic chloride and oxalic acid of various compositions.

EXPERIMENTAL

A solution of Schuchardt's stannic chloride crystals was prepared by dissolving an approximately weighed quantity in Merck's dilute

hydrochloric acid solution of known concentration. The solution was carefully estimated by gravimetric method, and diluted and hydrochloric acid added to get a solution of exactly decimolar stannic chloride in normal hydrochloric acid. Hydrochloric acid was needed to prevent hydrolysis. This solution of stannic chloride in hydrochloric acid has been referred to in this paper as stannic chloride solution. Standard solutions of AnalaR oxalic acid were also prepared.

The absorption spectra of individual solutions and also those of the mixtures were photographed as described below. For photographing the spectra Adam Hilger's Constant Deviation Quartz Spectrograph was used with copper are as the source. The photographs were taken on Ilford Empress Plates and an exposure of one minute was allowed in each case. Different thicknesses of the solutions were used for absorption of the radiations by means of a Baly's tube. The experiments were performed at a temperature of 25° C. From the photographs the regions of absorption corresponding to the different thicknesses of the various solutions employed were read. The results are recorded below :

TABLE I

Region of Absorption A.° U

Thickness of Solution	*Plate* 1 M/2HCl	*Plate* 2 M/20 $SnCl_4$	*Plate* 3 M/4 $H_2C_2O_4$	*Plate* 4 M/10 $SnCl_4$ + M/2·0 $H_2C_2O_4$	*Plate* 5 M/10 $SnCl_4$ + M/2·25 $H_2C_2O_4$	*Plate* 6 M/10 $SnCl_4$ + M/2·5 $H_2C_2O_4$	*Plate* 7 M/10 $SnCl_4$ + M/3·0 $H_2C_2O_4$	*Plate* 8 M/10 $SnCl_4$ + M/3·5 $H_2C_2O_4$	*Plate* 9 M/10 $SnCl_4$ + M/4·0 $H_2C_2O_4$	*Plate* 10 M/10 $SnCl_4$ + M/5·0 $H_2C_2O_4$	*Plate* 11 M/10 $SnCl_4$ + M/8·0 $H_2C_2O_4$	*Plate* 12 M/10 $SnCl_4$ + M/10 $H_2C_2O_4$	*Plate* 13 M/10 $SnCl_4$ + M/20 $H_2C_2O_4$	*Plate* 14 M/10 $SnCl_4$ + M/40 $H_2C_2O_4$
18mm	2618	2618	3050	3000	3000	2950	2950	2950	2880	2880	2880	2840	2618	2618
16	2618	2618	3050	3000	3000	2950	2950	2880	2880	2880	2840	2840	2618	2618
14	2618	2550	3050	3000	3000	2880	2880	2880	2880	2880	2840	2840	2618	2618
12	2618	2550	3050	3000	3000	2880	2880	2880	2880	2880	2840	2618	2618	2618
10	2550	2550	2890	2880	2880	2880	2880	2880	2880	2800	2618	2618	2618	2618
8	2550	2500	2890	2880	2880	2880	2880	2880	2800	2800	2520	2520	2520	2618
6	2550	2500	2890	2780	2780	2700	2700	2840	2800	2450	2490	2490	2520	2520
4	2550	2460	2770	2780	2780	2700	2700	2618	2450	2450	2450	2490	2470	2480
3	2520	2460	2770	2780	2780	2618	2618	2450	2450	2450	2425	2425	2470	2480
2	2520	2460	2618	2618	2618	2450	2450	2400	2425	2400	2425	2425	2450	2480
1	2520	2425	2425	2618	2350	2350	2350	2350	2350	2350	2350	2425	2325	2400

Discussion of Results

For the interpretation of the absorption spectra results the shifts in the line 2618 A°.U. were considered. The thicknesses of solutions of different compositions required to produce absorption upto this region are tabulated below.

TABLE II

Ratio $Sn^{IV} : C_2O_4^{--}$	Thickness of solution in mm
1 : 0	18 – 16
1 : 0·25	18 – 8
1 : 0·50	18 – 10
1 : 1·00	12 – 10
1 : 1·25	10
1 : 2·00	5·4
1 : 2·50	5·4
1 : 2·86	4
1 : 3·33	3
1 : 4·00	3
1 : 4·44	2
1 : 5·00	2
1 : ∞	2

A graph was then plotted showing the change in the required thicknesses with change in compositions of the mixture. A perusal of the curve shows that the first break in the curve occurs at the point corresponding to 2 of oxalate for 1 of tin, and this point may, therefore, be assigned to the formation of normal stannic oxalate. As the formation of stannic oxalate is complete, complex formation seems to commence and the formation of the complex is finally complete at 4 of oxalate for 1 of tin, where there is the last break in the curve and then the curve smoothly parallel to the axis. Thus we conclude that the absorption spectra also leads us to the inference of the formation of $Sn(C_2O_4)_2$ and $H_4Sn(C_2O_4)_4$ in a mixture of solutions of stannic chloride and oxalic acid, which

is in agreement with the results arrived at by the electrical conductivity of stannic hydroxide-soluble oxalate system, as reported in a previous part of the series.

References

1. Dey (1946): *University of Allahabad Studies*, **22**, 7
2. Dey and Bhattacharya (1945): *Current Science*, **14**, 69
   (1946): *Proc. Nat. Acad. Sci.*, India, **15**, 86
3. Dey (1947): *Ibid*, **16**, 27
4. Dey and Bhattacharya (1948): *J. Ind. Chem. Soc.*, **25**, 571
5. Dey (1948): *J. Colloid Sci.*, **3**, 473

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART IV] SECTION A [VOL. 18

"NOTE ON THE HARMONIC POLARS AND THE CAYLEYAN OF A CUBIC"

By

HARIDAS BAGCHI, M. A., PH. D.,
(Offg.) Head of the Department of Pure Mathematics, Calcutta University
Received on 5.5.49

ABSTRACT

The main object of the present investigation is to reckon with the special geometrical relations, that connect any of the nine harmonic polars of a (bicursal) cubic Γ and its Cayleyan (or Pippian Ω), (which is naturally a curve of the 6th order and 3rd class). O being any of the nine inflexions of Γ, L being the *related* harmonic polar and K being the point where L meets the (inflexional) tangent at O, the following properties represent some of the *novel* results arrived at in this paper:—

(a) that the line-pair (M, N), (representing the *degenerate* polar conic of K), taken in conjunction with the inflexional tangent OK, makes up the triad of tangents, that can be drawn from O to the class cubic—Ω;

(b) that P, Q, being the two points where L cuts the lines, M, N, respectively, the six points of intersection of L with the order sextic Ω consist of

(i) the points P, Q, K (each counted *singly*)
and (ii) a certain cusp (on L), (counted *thrice*),
(the cuspidal tangent being no other than the line L itself);

(c) that the osculating conics of Γ at the three ('cognate') sextactic points, lying on L, possess a *common* self-conjugate triangle which is in a sense *circumscribed* about the Cayleyan Ω;

and (d) that the common self-conjugate of (c) is no else than the Δ OPQ. By the way, it may be remarked that the propositions (a), (b), (c) and (d) have been demonstrated in such a way as to throw a *new* light on a certain result, proved in the first instance in the author's "*Note on Conics of double osculations*" (to be published in the next issue of the '*Journal of the National Academy of Sciences*', Allahabad).

INTRODUCTION

The main purpose of the present paper is to scrutinise the peculiar geometrical relations, that subsist between any of the nine harmonic polars of a (bicursal) cubic and its Cayleyan. Incidentally certain special tangents of the Cayleyan have been reckoned with, and the *common* self-conjugate triangle of a triad of 'cognate' sextactic conics has been talked about and discussed in such a way as to give prominence to the relation, which it bears to the polar conic of the (associated) point of contact of the Cayleyan and the Hessian of the (original) cubic. For the sake of clearness and easy reference, certain results, established in my "Note on conics of double osculation of a cubic" have been re-stated in this paper. The greater part of the results arrived at in this paper is believed to be original.

SECTION I

(*Certain novel properties of a triad of cognate sextactic conics.*)

Art. 1. It is common knowledge that a bicursal cubic has, in general

(i) 9 points of inflexion $\{I_r\}$,

(ii) 9 associated harmonic polars $\{L_r\}$.

and (iii) 27 sextactic points, lying, three by three, on the 9 lines $\{L_r\}$. For felicity of expression, two or three sextactic points, seated on the *same* harmonic polar, will be said to be 'cognate' to one another, and their attached osculating (*i. e.*, six-pointic) conics will be similarly termed 'cognate'. Naturally, then, a (bicursal) cubic possesses altogether 9 triads of 'cognate' sextactic conics (real or imaginary). The investigation of the peculiar geometrical relations, subsisting amongst

the three sextactic conics of any of the nine '*cognate*' triads is the main objective of the present section. For this purpose Cartesian analysis, involving the use of oblique axes, will be resorted to in the succeeding article.

Art. 2. Suppose that any one of the points of inflexion $[I_r]$ of a given bicursal cubic Γ is chosen as the origin O of Cartesian coordinates, and that the tangent to Γ at O is chosen as the axis $(y=0)$. If, then, α be one of the three sextactic points (of Γ), that have O for their tangential, and the line $O\alpha$,—which is after all one of the tangents from O to Γ—be taken as the axis $(x=0)$, the Cartesian equation to Γ can be readily thrown into the form :

$$S.y = x^3, \qquad \ldots \quad \text{(I)}$$

where $S \equiv ax^2+2hxy+by^2+2gx+2fy+c=0$, $(A \equiv bc-f^2=0)$ ... (II)
is the osculating (*i.e.*, six-pointic) conic of Γ at α. It goes without saying that the Cartesian axes, chosen as above, are in general oblique.

If we now re-write (I) in the form :

$$(S+3\lambda x^2+3\lambda^2xy+\lambda^3y^2)\,y=(x+\lambda y)^3, \qquad \ldots \quad \text{(III)}$$

and prescribe the condition that the line

$$x+\lambda y=0$$

may touch the conic

$$\left.\begin{array}{l} S+3\lambda x^2+3\lambda^2xy+\lambda^3y^2=0, \\ \textit{i.e.,}\quad (a+3\lambda)x^2+2(h+\tfrac{3}{2}\lambda^2)xy+(b+\lambda^3)y^2+2gx+2fy+c=0, \end{array}\right\} \quad \ldots \text{(IV)}$$

we gather

(i) that the other two sextactic conics S_1, S_2, '*cognate*' with S are given by

$$S_1 \equiv (a+3\lambda_1)x^2+2(h+\tfrac{3}{2}\lambda_1^2)xy+(b+\lambda_1^3)y^2+2gx+2fy+c=0 \quad \ldots \text{(V)}$$

and $S_2 \equiv (a+3\lambda_2)x^2+2(h+\tfrac{3}{2}\lambda_2^2)xy+(b+\lambda_2^3)y^2+2gx+2fy+c=0$ ...(VI)
and (ii) that the associated sextactic points β and γ—naturally 'cognate' with α—are respectively

$$\left(\frac{\lambda_1}{f-\lambda_1 g}, -\frac{1}{f-\lambda_1 g}\right) \text{and} \left(\frac{\lambda_2}{f-\lambda_2 g}, -\frac{1}{f-\lambda_2 g}\right), \qquad \ldots \quad \text{(VII)}$$

provided that the two parameters λ_1, λ_2 are the roots of the quadratic in λ, viz.,

$$A\lambda^2+B\lambda+2H=0. \qquad \ldots \quad \text{(VIII)}$$

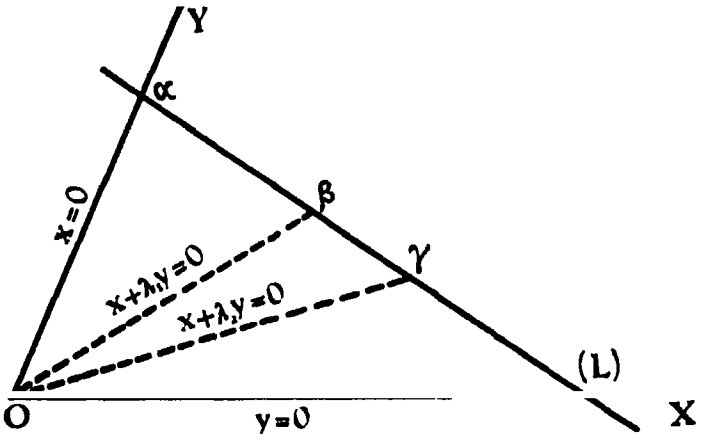


Fig. 1.

As is to be expected, the three 'cognate' sextactic points α, β, γ are situated on the line:

$$gx+fy+c=0,$$

which is none other than the harmonic polar L, appertaining to the inflexion O.

Appeal to algebraic reasoning makes it plain that the three '*cognate*' sextactic conics S, S_1, S_2 are representable by the *single* Cartesian equation :

$$S+\lambda\left(3x^2-\frac{2H}{c}y^2\right)+\lambda^2\left(3xy-\frac{By^2}{c}\right)=0, \quad . \quad . \quad . \quad \text{(IX)}$$

it being tacitly understood that the parameter λ is to take on the values $0, \lambda_1, \lambda_2$ in succession.

Art. 3. Because the Jacobian of any three curves of the *net*:

$$lU+mV+nW=0$$

(where U, V, W are given curves and l, m, n are parametric constants) is the same as that of U, V, W, we infer immediately from (IX) of the preceding article that

$$J(S, S_1, S_2)$$

is the same as the Jacobian of the three conics

$$S=0, \quad 3x^2-\frac{2H}{c}y^2=0 \text{ and } 3xy-\frac{By^2}{c}=0,$$

and has therefore for its Cartesian equation

$$\begin{vmatrix} ax+hy+g, & hx+by+f, & gx+fy+c \\ 3x \quad , & -\frac{2H}{c}y \quad , & 0 \\ 3y \quad , & 3x-\frac{2B}{c}y \quad , & 0 \end{vmatrix} = 0.$$

This determinantal equation being equivalent to

$$(gx+fy+c)\ (3cx^2-2Bxy+2Hy^2)=0,$$

the logical conclusion is that the Jacobian of the three 'cognate' sextactic conics S, S_1, S_2, appertaining to the point of inflexion O, consists of the related harmonic polar L, viz.,

$$gx+fy+c=0, \qquad \ldots \quad (1)$$

and the line-pair (M, N) defined by

$$3cx^2-2Bxy+2Hy^2=0. \qquad \ldots \quad (2)$$

That the first line viz., L should form a part and parcel of the degenerate cubic

$$J\ (S, S_1, S_2)$$

could be foreseen from geometrical considerations It now remains to scrutinise the geometrical features of the other two lines M, N.

At the very outset we note that the three pairs of tangents, that can be drawn from O to the three conics S, S_1, S_2, as defined by (IX) of the foregoing article, are representable by the *single* Cartesian equation:

$$(B+3c\lambda)x^2-2\ (H-3/2\ c\lambda^2)xy+c\lambda^3y^2=0, \qquad \ldots \quad (3)$$

provided that the parameter λ is allowed to assume the values 0, λ_1, λ_2 in succession.

Recognising, then, that the (necessary and sufficient) condition for the two pairs of lines (2) and (3) to be harmonically conjugate is that λ should satisfy the cubic equation :

$$c\lambda^3+B\lambda^2+2H\lambda=0,$$

so that the admissible values of λ are, by (VIII) of Art. 2, 0, λ_1, λ_2, we come to conclude that the three pairs of tangents that can be drawn from O to S, S_1, S_2 respectively, constitute an involutory system, of which the two focal lines are determined by (2). Hence,

bearing in mind that the harmonic polar L is the common polar (line) of the point O *w.r.t.* the three conics S, S_1, S_2, we readily realise that the line L must intersect the three conics in (three) pairs of points, forming an involution of which the two foci (or double points) P, Q are the two points where L cuts M, N respectively.

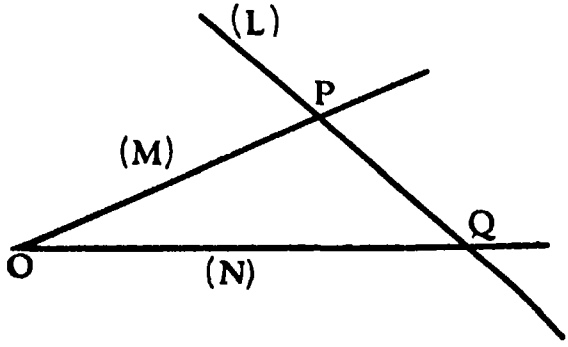


Fig. 2.

Because the polar of P *w. r. t.* any of the three conics (S, S_1, S_2) goes through both O and Q, and the polar of Q similarly goes through both O and P and the polar of O (viz., L) goes through P, Q, we are squarely led to the following proposition* :—

The cognate sextactic conics (S, S_1, S_2), *attaching to any of the nine points of inflexion of a bicursal cubic, possess a common self-conjugate triangle whose sides are the three line-constituents of the degenerate Jacobian* (S, S_1, S_2).

In Sec. II we shall discuss, among other things, certain novel geometrical properties of the line-pair (M, N).

SECTION II

(*Harmonic polars and other special tangents of the Cayleyan*).

Art. 4. If we now look back upon Art. 2 and adhere to the same notations and conventions, we may, as before, represent a given bicursal cubic Γ in the Cartesian form

$$Sy = x^3 \qquad \ldots \quad (I)$$

* It may be incidentally remarked that the proposition proved above is but a particular phase of a *more general* proposition, proved by me in my paper on "*Conics of double osculation of a cubic.*" The method, adopted in that paper, is *general*, whereas the method outlined as above, is rather *special*, fitting in with the restricted case.

provided that one of the points of inflexion of Γ is taken as the origin O and the tangent to Γ at O is taken as the axis ($y=0$) and one of the three tangents (say, $O\alpha$) that can be drawn from O to Γ is taken as the axis ($x=0$), and the osculating (*i.e.*, six-pointic) conic of Γ at the point of contact α of this tangent is taken in the form :

$$S \equiv ax^2+2hxy+by^2+2gx+2fy+c=0, \ (A \equiv bc-f^2=0). \quad . \quad . \quad . \quad (II)$$

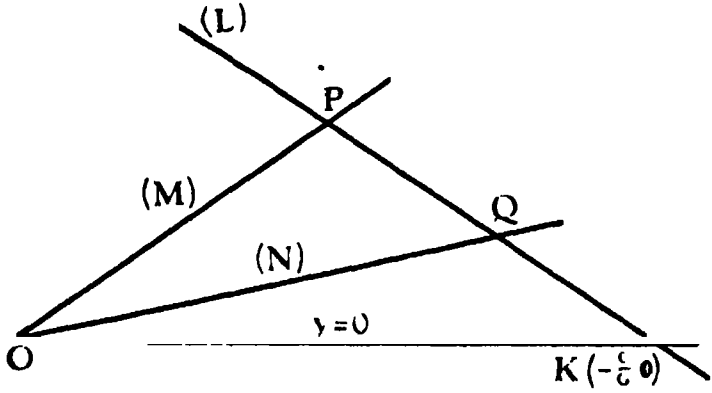


Fig. 3

Harmonic polar ($gx+fy+c=0$)

Since the harmonic polar L of the inflexion O is

$$gx+fy+c=0,$$

the point K, where L meets the inflexional tangent ($y=0$), is

$$\left(-\frac{c}{g}, 0\right),$$

and the polar conic of this point *w. r. t.* Γ is easily seen to be

$$3cx^2-2Bxy+2Hy^2=0.$$

This being the same as (2) of Art. 3, the inevitable conclusion is that the line-pair (M, N), considered in Art. 3, is designable as the (degenerate) polar conic of the point K. A part of this result could have been anticipated from general considerations. For the polar conic of the inflexion O being compounded of two lines (viz., the inflexional tangent and the harmonic polar L) crossing each other at K, the polar conic of K must reciprocally be a pair of lines, crossing each other at O.

We may now, on the strength of other results proved heretofore, summarise our conclusions in the form of a theorem:—

THEOREM A. *The* 27 *sextactic conics of a bicursal cubic* Γ *can be distributed into* 9 *triads of 'cognate' conics, attaching respectively to the* 9 *points of inflexion* $\{I_r\}$, $(r=1, 2, \ldots\ldots 9)$. *Further the three 'cognate' (sextactic) conics related to any of the* 9 *points of inflexion (say,* I_r*), possess a common self-conjugate triangle, whose sides consist of the harmonic polar* (L_r) *of* I_r *and the two line-constituents of the (degenerate) polar conic (w. r. t.* Γ*) of the point* K_r *(on the Hessian), conjugate to* I_r.

Relying upon the known lemma that the system of polar conics (*w. r. t.* a given bicursal cubic Γ) of the ∞^1 points, situated on a given right line (say, Λ) form a 'pencil', whose four *common* points are the (four) poles of Λ, we promptly perceive, on referring to Fig. 3, that the four poles of the inflexional tangent OK are the four points of intersection of the two line-pairs :

$$(OK, L) \text{ and } (M, N).$$

Hence the four poles of OK consist of

O (counted twice),

and P, Q (each counted once).

We may accordingly enunciate Theorem A in the following modified form:—

THEOREM B. *The* 27 *sextactic conics of a bicursal cubic* Γ *can be divided into* 9 *triads of 'cognate' conics, attaching respectively to the* 9 *points of inflexion* $\{I_r\}$. *Furthermore the three 'cognate' (sextactic) conics of the triad related to any particular point of inflexion* (I_r) *admit of a common self-conjugate triangle, whose vertices are the three distinct poles of the (inflexional) tangent to* Γ *at* I_r.

Art. 5. Referring again to Fig. 3 we notice that O, K being a pair of '*conjugate poles*' on the Hessian Γ', the joining line OK must be a tangent to the Cayleyan ($\mathfrak{a}$). Besides, each of the two lines M, N (*i. e.*, OP, OQ) must be a tangent to $\mathfrak{a}$, seeing that the two lines, taken together, constitute a *degenerate* polar conic of Γ (Art. 4). Thus

OP, OQ and OK must all touch Ω Now Ω must be a curve of the third class and sixth degree, for Γ is a *bicursal* cubic. So we have in a way ascertained all the *three* tangents (*viz.*, OP, OQ, OK) that can possibly be drawn from the point O to the *class-cubic* Γ.

If we now look for the *actual* points of contact (with Ω) of the tangents OP, OQ, OK as also L, we have to bank upon the following wlel-known lemmas* of Higher Plane Curves, *viz.*,

(*i*) that, if γ, δ be a pair of conjugate poles on the Hessian Γ' of a (bicursal) cubic Γ, the four points of contact, (with the Cayleyan Ω) of the two line-pairs, representing the degenerate polar conics of γ, δ will lie on a right line (say, Σ) ; and

(*ii*) that the line-pair (Σ, $\gamma\delta$) constitutes the degenerate polar conic of the *third centre* of the quadrangle, formed by the four poles of the line $\gamma\delta$ (the other two centres being, of course, the points γ, δ themselves).

What is needed now is to apply the two lemmas (*i*) and (*ii*) to the special pair of 'conjugate poles' (on Γ'), *viz.*, O and K.

In the concluding portion of the previous article it has been shewn that the quadrangle, made up of the four poles of the line OK reduces practically to a triangle *viz.*, OPQ, so that the three centres of this *degenerate* quadrangle consist of

O (counted twice) and K

Consequently, the *third* centre of the quadrangle—as contemplated in lemma (*ii*)—is none other than the point of inflexion O, whose (degenerate) polar conic is the line-pair (OK, L).

---

*Vide Basset's '*Cubics and Quartics*' (1st edition) Art. 119 (Ch. V),

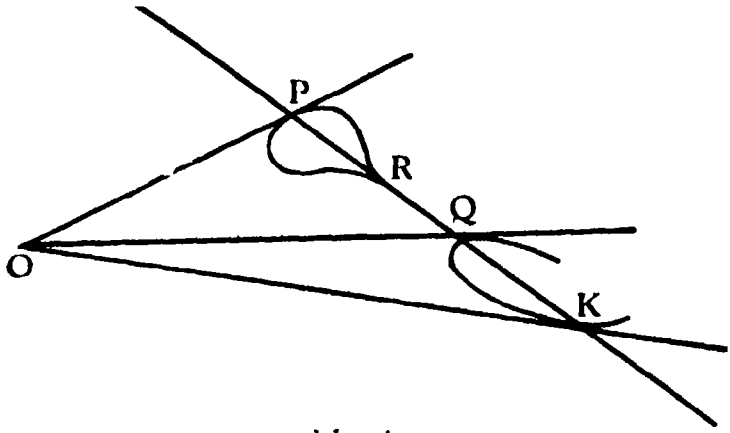


Fig. 1.

Hence the line of collinearity—as guaranteed by lemma (i)—of the four points of contact (with Ω) of the four lines

$$OP, \quad OQ, \ (OK) \text{ and } L \qquad \ldots \quad (I)$$

is the right line L. Palpably, then, the actual points of contact of these lines (with Ω) are respectively

$$P, Q, K \quad \text{and} \quad R, \qquad \ldots \quad (II)$$

the last-named point R, being, of course, a *cusp* (of Ω), the tangent where at is the harmonic polar L. The adjoining fig. 4 gives a rough idea of the configuration of the several points and lines, that figure in the above discussion.

Apropos of this, it may be remarked that, being an order-sextic Ω must cut an arbitrary right line—not excepting L—at *six* points (real or imaginary). What has been proved heretofore indirectly amounts to saying that *the six points of intersection of the harmonic polar L with the Cayleyan consist of the cusp R (counted thrice) and the three simple points P, Q and K.* It is scarcely necessary to add that similar properties must hold in respect of the hexad of intersections of the Cayleyan Ω with each of the remaining eight harmonic polars.

Now according to a well-known lemma, the line OK touches the Hessian Γ' at the point K, so that Γ' and Ω touch each other at K, the common tangent thereat being OK. Inasmuch as each of the three sides of the triangle OPQ touches Ω (the three points of contact being

located on the side PQ), we may, *in a special sense*, speak of OPQ as a triangle, circumscribed about Ω. Hence we are justified in re-stating Theorem A or Theorem B in the following alternative form:—

Theorem C. *The* 27 *sextactic conics of a bicursal cubic* Γ *can be arranged into* 9 *distinct triads, associated respectively with the* 9 *inflexions of the type* $\{I_n\}$. *Further the three 'cognate' (sextactic) conics, belonging to each of these triads, possess a self-conjugate triangle, circumscribed about the Cayleyan.*

STUDIES IN THE OPTICAL ROTATION OF ABIETIC ACID.

Part I Optical rotation in cyclohexane and its derivatives.

S P. MITRA

(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALLAHABAD.)

(Received on July 7, 1949)

The work on the chemistry of rosin dates back to 1826 when Baupe[1] first showed that it contained crystallizable acids. A large amount of work has since been published on the rosin acids and on their relation to the original composition of rosin. Acids of different physical properties have been isolated by different investigators and variously named abietic, pimaric, sylvic, sapinic etc. The empirical formula of these acids were first determined as $C_{20}H_{30}O_2$ by Trammsdorf[2]. Kemner[3] found that the chief constituent of French rosin is pimaric acid whereas the chief constituent of American rosin is abietic acid. Mitra and Ghatak[4] and Rau and Simonsen[5] have established that abietic acid is the chief constituent of Indian rosin from *Pinus longifolia*. The physical properties of abietic acid depend upon the method of preparation and purification but the chemical properties are independent of the same[6].

Abietic acid was prepared from the best quality Water White rosin from *Pinus longifolia* from Jallo Rosin & Turpentine Factory, Lahore, by distillation in super-heated steam[4]. Great care was taken to use freshly powdered sample of rosin. for powdered rosin on storage gets oxidised.

M. P. 160-63°C

Anal:	Calculated for $C_{20}H_{30}O_2$	C—79·47	H—9·93.
	Found	C—79·02	H—10·22.

The acid was stored as sodium tetra-abietate and was regenerated as needed from the salt.

Paul Drude[7] gave a general equation for rotatory dispersion

$$[\alpha] = \Sigma \frac{K}{\lambda^4 - \lambda_0^4}.$$

Each term of the summation has two constants, K (rotation constant) and λ_0^2 (Dispersion constant).

Rotatory dispersion may be classified as "Simple" or "Complex" accordingly as they can or cannot, be expressed by Drude's one term equation

$$[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}.$$

The abietic acid isolated from Indian rosin was found to obey the simple dispersion formula exactly in solutions in cyclohexane and its derivatives.

Very pure samples of solvents were used in these experiments and the solvents were further purified by distillation. Exact straight lines were obtained (Fig. 1.) when $1/[\alpha]$ was plotted against λ^2. This is a sufficient proof of the rotatory dispersion being simple. But more stringent numerical tests have been applied and the values are recorded in tables 2 and 3. The difference between the observed rotatory power (o) and that calculated (c) from the dispersion equation are within the limits of experimental error allowed in such measurements.

Generally the deviations lie between $\pm 0{\cdot}03°$ but for Hg_{4916} a difficult line to read, this difference lies between $\pm 0{\cdot}09°$.

The specific rotatory power of abietic acid for Hg_{4358} in different solvents are given in table 1.

The influence of the solvent on the rotation of an optically active substance has been the subject of repeated investigations. Walden[8]

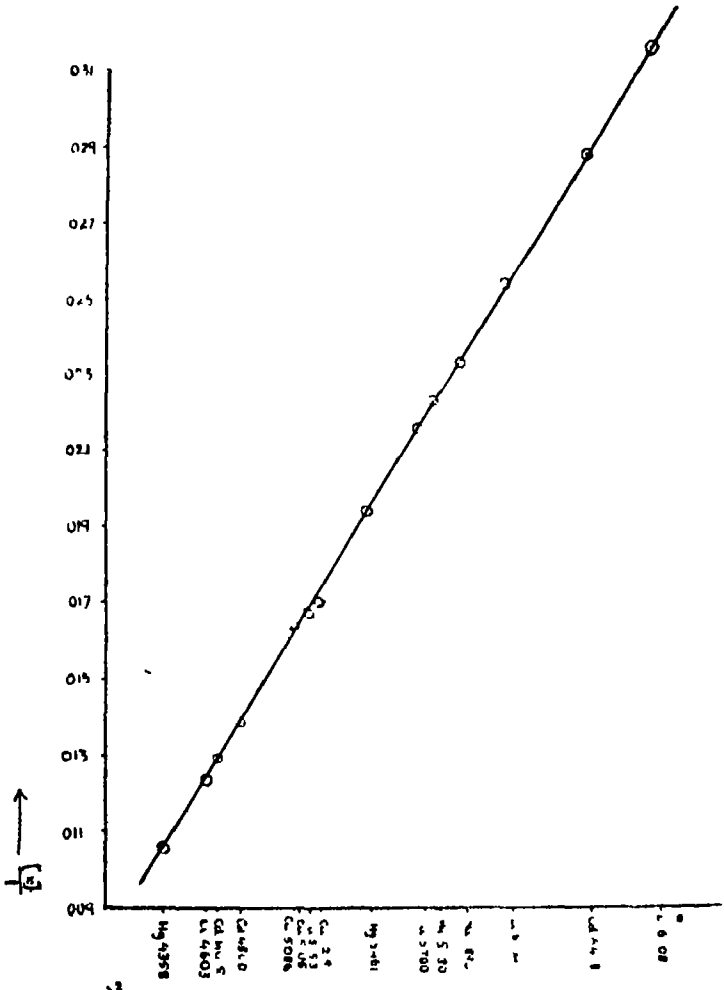


FIG - I

established that there exists a connection between the osmotically determined molecular size and of the active solute and its rotation in the same solvent. The relationship between the degree of association and the rotation is not, however, revealed in a simple parallelism but each constituent of the solution exercises a constitutive influence on the value of rotation. Nernst[9] and Meldrum and Turner[10] showed that the dielectric constant of the solvent was the controlling factor on optical rotation apart from any chemical action.

Table 1

Solvent	Dielectric constant	$[\alpha]^{25°}_{5461}$	K	λ_0 A°.U	Dispersion ratio $\frac{\alpha_{4358}}{\alpha_{5461}}$
1. Cyclohexane	2 05	—21·46	5·14	2429	1·831
2. Methyl cyclohexane ..	2·10	—18·22	4 34	2436	1·825
3. Cyclohexanol ...	15·00	— 62·04	14 86	2426	1·829
4. Methyl cyclohexanol ..	.	—61·28	14 69	2419	1 825
5 Cyclohexanyl acetate ..	..	—49 10	11·75	2429	1·826
6. Methyl cyclohexanyl acetate ...		—44·95	10·75	2431	1·829
7. Cyclohexanone	18·20	—66 07	15·79	2429	1 826
8. Methyl cyclohexanone .	.	61·97	14 88	2410	1·817

Rule[11] found that an increase in polarity of the solvent decreases the rotatory power, although for some optically active compounds the reverse occur.

According to Debye dipole association occurs between the polar molecules. When association of this kind occurs between a dipole in the optically active solute and another in the solvent, the field of force within the active molecules will be weakened and the contribution of the dipolar radical to the total optical activity of the molecule will be reduced. The more powerful the dipoles in the solvent, the greater will be the degree of dipole association between the solute and the solvent and the greater the observed change in optical rotation. With weakly polar solvents, solvation may lead to a tendency for the solvent dipoles to become loosely oriented towards the solute molecules giving rise to minor effects of the same kind.

Temperature – 25°C

Solvent	Cyclohexane			Methyl cyclohex	
Concentration grams/100 c.c.	2 4424			2 4420	
Calculated $[\alpha]$	$-\frac{5\ 141}{\lambda^2-0\ 05900}$			$-\frac{4\ 346}{\lambda^2-0\ 05934}$	
Calculated λ_0	0 2429			0 2436	
Line λ	Obs [α]	Cal [α]	Diff o c	Obs [α]	Cal [α]
Hg 4358	−39 30	−39 25	+0 05	−33 26	33 29
Li 4603	33 64	33 66	−0 02	28 52	28 51
Cd 4678	32 14	32 15	−0 01	27 26	27 23
Cd 4800	30 03	30 00	+0 03	25 37	25 41
Cd 5086	25 76	25 74	+0 02	21 84	21 79
Cu 5106	25 53	25 49	+0 04	21 55	21 58
Cu 5153	24 90	24·88	+0 02	21 08	21 07
Cu 5219	24 11	24 09	+0 02	20 44	20 39
Hg 5461	21 46	21 49	−0 03	18 22	18 19
Cu 5700	19 35	19 33	+0 02	16 32	16 36
Hg 5780	18 72	18 69	+0 03	15 80	15·81
Na 5893	17 88	17 85	+0 03	15 06	15 09
Li 6104	16 40	16 41	−0 01	13 90	13 87
Cd 6438	14 50	14 47	+0 03	12 30	12 24
Li 6708	13 11	13 15	−0 04	11 12	11 13
	No mutarotation			No mutarotat	

The sequence of decreasing rotatory power of abietic acid in cyclohexane and its derivatives are as follows : Cyclohexanone > Methyl cyclohexanone > Cyclohexanol > Methyl cyclohexanol > Cyclohexanyl acetate > Methyl cyclohexanyl acetate > Cyclohexane > Methyl cyclohexane.

The sequence of decreasing or increasing rotatory power does not run strictly parallel with that of the dielectric constants of the solvents. In spite of this some parallelism can be tracted between the rotatory power of abietic acid and the dielectric constants of the solvents in which the rotatory power is determined.

The above mentioned sequence of decreasing rotatory power in different solvents are derived from the rotatory power data for Hg_{5461} (Table 1). The choice of this wavelength is purely arbitrary. The same sequence was found to hold good for abietic acid with other wavelengths. But this is not true for all optically active substances It is, therefore, necessary for any strict comparison of rotatory power of a series of compounds that the effects of dispersion should be eliminated. This elimination is neither very easy nor very safe when the dispersion is complex, but when a linear relation is found to hold good as in this case, the extrapolation is both simple and accurate. In this case when the simple dispersion formula holds good, the effects of dispersion can be eliminated completely by using the rotation constant K of the one term equation of Drude as a measure of the absolute rotatory power of the medium. It refers to a wavelength λ where $\lambda^2 - \lambda_0^2 = 1$ square micron and is not much greater than 10,000 A. U. The longest observed wavelength in these measurements Li_{6708} and an extrapolation from it to about 10,000 A.U. is easily permissible in view of the linear nature of the dispersion equations obtained from these measurements. Hence the values of K, the rotation constant as a measure of the absolute rotatory power of the substance are given in table 1. It would be found that the sequence of rotation constant K is the same as the optical rotation.

λ_0^2, the dispersion constant in the Drude's equation represents the square of the wavelength of the dominant absorption band controlling the optical rotation.

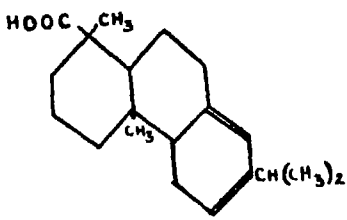
Pickard and Hunter [12] found that the rotatory dispersion of *d*-γ – nonyl nitrite could be expressed by the equation

$$\alpha = \frac{0{\cdot}76}{\lambda^2 - 0{\cdot}135} + \frac{0{\cdot}43}{\lambda^2}.$$

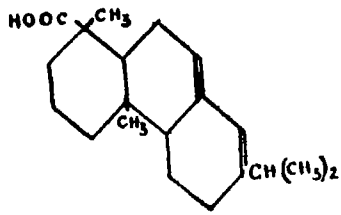
The dispersion constant $\lambda_0^2 = 0{\cdot}135$ corresponds with a characteristic wavelength $\lambda_0 = 3680$A. U. Direct measurements of absorption revealed a maximum at 3670 to 3720 A. U. in good agreement with the wavelength deduced from measurements of rotatory dispersion. It, thus, appears that the characteristic absorption bands which rotatory dispersion equations predict have a real existence

The characteristic absorption band λ_0 for abietic acid in different solvents as obtained from measurements of rotatory dispersion are given in table 1.

The structure I was assigned to abietic acid from a study of the oxidation products but Ruzicka, Sternbach and Jeger[13] produced the most unequivocal chemical evidence for structure II which is now generally accepted.



I



II

Confirmatory evidence for structure II is supplied by Woodward's calculations[14] of the absorption spectra for normal conjugated dienes (the double bonds not lying in one ring). λ_{max} (calculated) for struc-

ture II is 2420±5 A. U. and λ_{max} for abietic acid observed by different workers by actual measurements of absorption are given below.

Kraft[15]	2375 A. U.
Harris & Sanderson[16]	2410 A. U.
Sanderman[17]	2400 A. U.

The values of absorption maxima obtained from rotatory dispersion measurements are found to be in very good agreement with the values obtained by actual measurement of absorption and with that calculated by Woodward's method.

The dispersion ratio is found to remain constant at 1·826.

It has been first observed by Dupont, Rouin and Dubourg[18] that the specific rotation of the rosin acids depend not only on the solvent used but also on the concentration in the solvent. Georgi[19] also observed the same phenomena. More systematic work on this point was undertaken in this laboratory and the result obtained for the rotation of abietic acid in different solvents are represented graphically in Figures II, III & IV. All the rotations measured are for Hg_{5461} at 25°C.

It is well known that most organic acids like benzoic acid are very strongly associated even in a dilute solution. It has been found that the electronegative group COOH confers the power of association to organic acids. Dupont, Rouin and Dubourg[18] have found from cryoscopic measurements that abietic acid is associated in alcohols. Moreover alcohols have been found to be the best associating solvent. They are themselves associated in solutions and when they act as solvents have the power of influencing the associating power of organic acids dissolved in them although this effect is least with alcohols as compared with other associating solvent. Moreover, combination between solute and solvent also take place which has the effect of reducing the

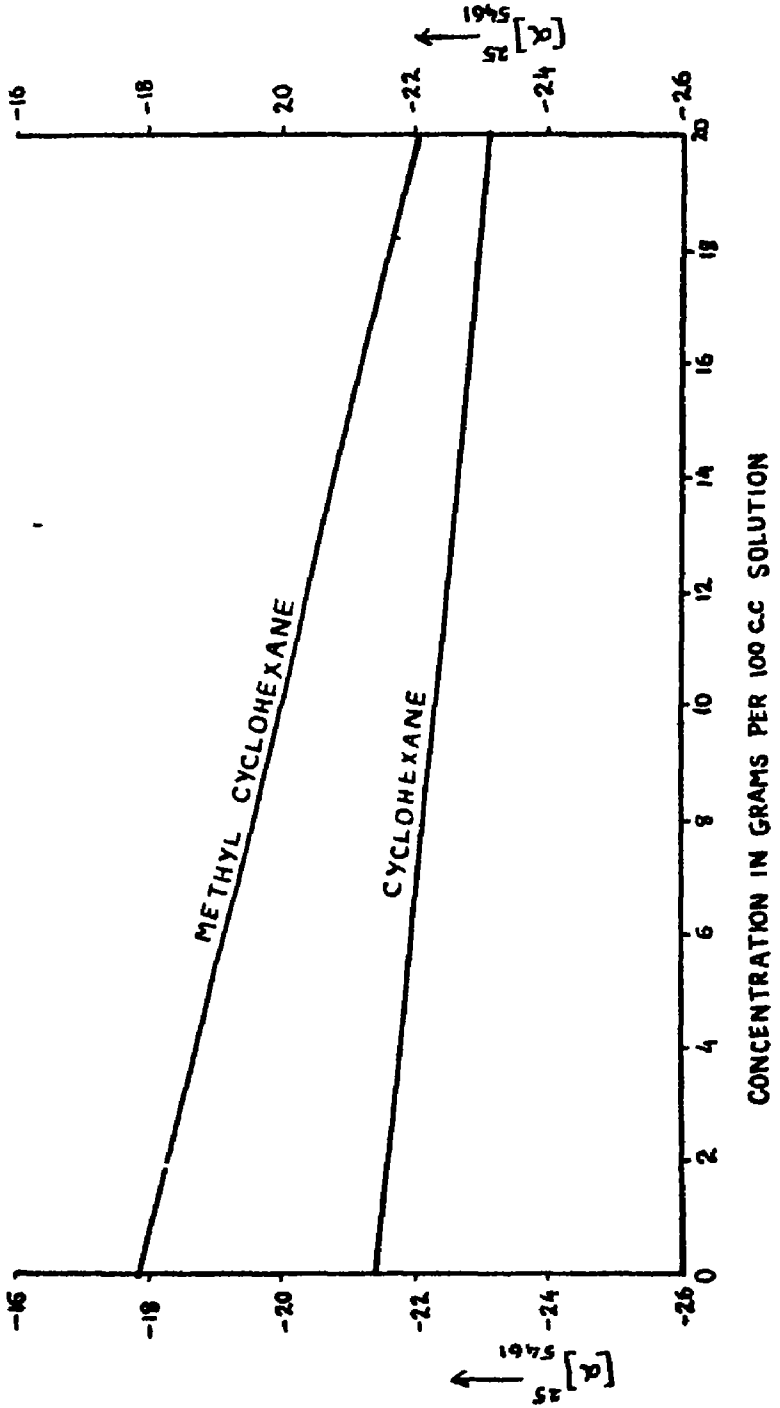

METHYL CYCLOHEXANE
CYCLOHEXANE
CONCENTRATION IN GRAMS PER 100 C.C SOLUTION
$[\alpha]^{25}_{5461}$
-16
-18
-20
-22
-24
-26
0
2
4
6
8
10
12
14
16
18
20

Fig-II

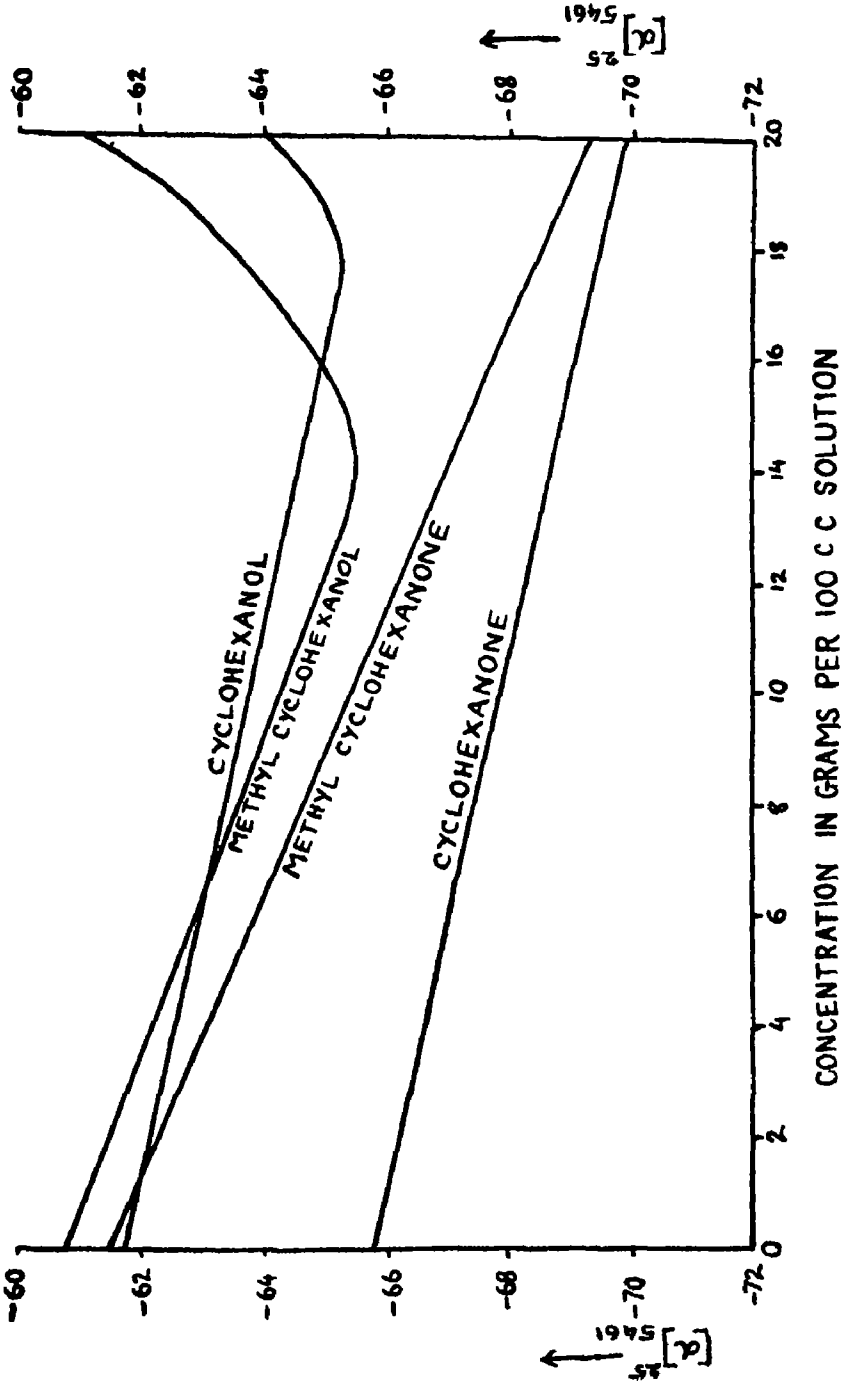

CYCLOHEXANOL
METHYL CYCLOHEXANOL
METHYL CYCLOHEXANONE
CYCLOHEXANONE
CONCENTRATION IN GRAMS PER 100 C C SOLUTION
$[\alpha]^{25}_{5461}$
-60
-62
-64
-66
-68
-70
-72
0
2
4
6
8
10
12
14
16
18
20

Fig -III

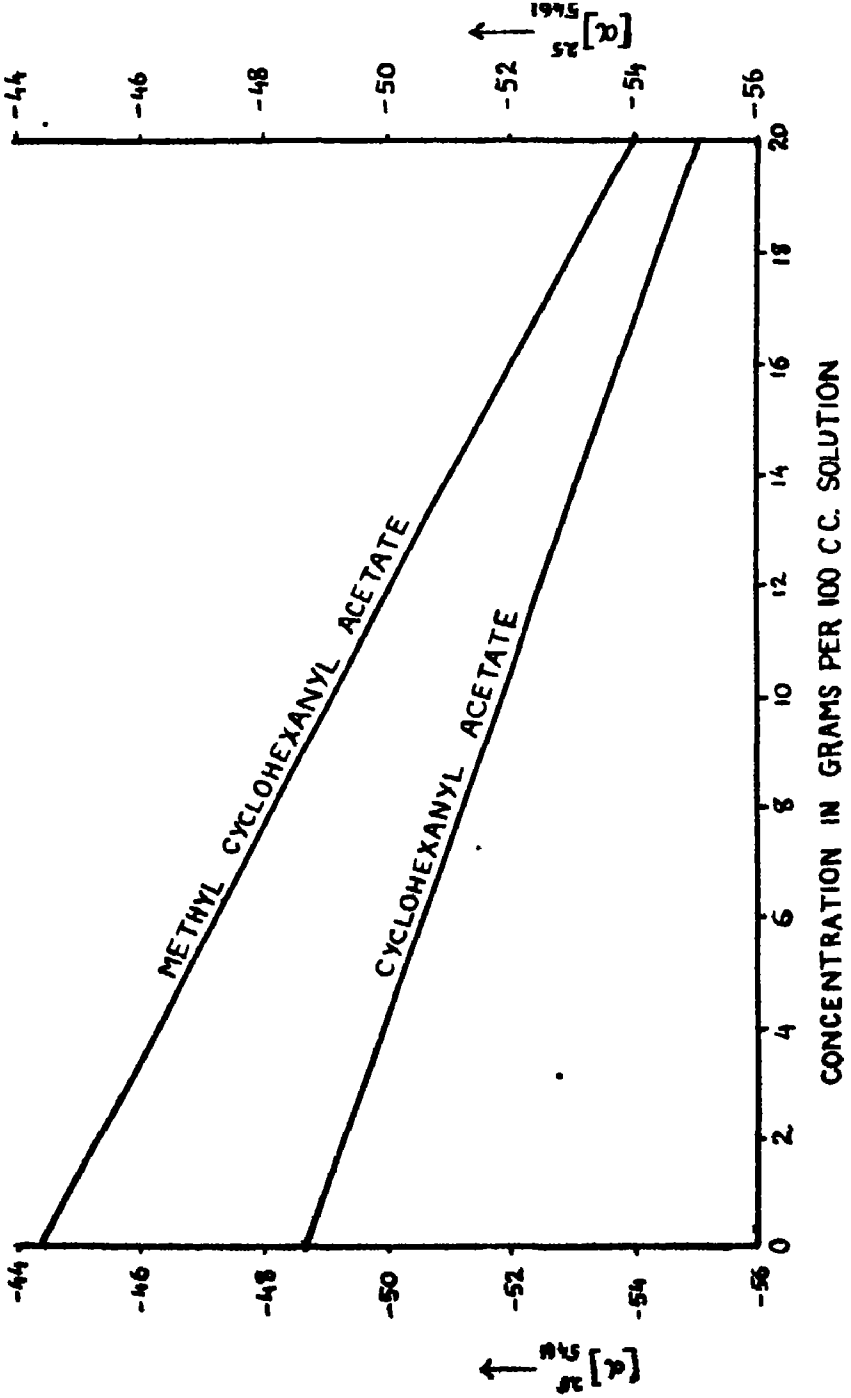

METHYL CYCLOHEXANYL ACETATE
CYCLOHEXANYL ACETATE
CONCENTRATION IN GRAMS PER 100 C.C. SOLUTION
-44
-46
-48
-50
-52
-54
-56
0
2
4
6
8
10
12
14
16
18
20

Fig -V

amount of free solvent thereby concentrating the solution leading to a change in optical rotation. The results obtained for the optical rotation of abietic acid can easily be explained on the above basis of association and compound formation and subsequent dissociation of the complex molecules. With Cyclohexane, Methyl Cyclohexane Cyclohexanone Methyl cyclohexanone, Cyclohexanyl acetate, Methyl cyclohexanyl acetate there is a gradual increase of specific rotation with increasing concentration. But with cyclohexanol and Methyl cyclohexanol there is a gradual increase of specific rotation with increasing concentration up to a certain limit beyond which the specific rotation decreases. This point corresponds where the dissociation of complex molecules between solute and and solvent begins.

References

1. Ann Chim. phys. 1826, 108.
2 Ann. Pharm **13**, 169, (1835)
3. Farben Ztg. **41**, 889, (1936).
4. J. Sci. & Ind. Res. **4**, 653, (1946).
5. Ind. Forest Records **2**, Part 6, (1926)
6. Chem Ztg. **34**, 149, (924).
7. The Theory of Optics, Leipzig, (1900).
8. Ber. **38**, 345, (1905).
9. Zeit. phys. Chem. **13**, 535, (1894).
10 Trans. Chem. Soc. **93**, 876, (1908).
11. J. Chem. Soc. **125**, 2155, (1924)
12. J. Chem. Soc. **123**, 434, (1923).
13. Helv. Chim. Acta **24**, 504, (1941).
14. J. Am. Chem. Soc. **64**, 72, (1942).
15. Ann. **520**, 133, (1935).

16 J Am Chem Soc 70, 334, (1948)

17 Ber 74, 154, (1941)

18. Bull. inst pin No, 38, 157 62 (1927).

19 Am Soc Test Materials 38, Part II, 498 (1938)
J Chem Ed 10, 415, (1933)

28 JUL 1981
NEW DELHI

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PARTS V & VI] SECTION A [VOL. 18

ABSORPTION MEASUREMENTS AT LOW FREQUENCIES IN SOME LIQUIDS

By

GURDEVA SHARAN VERMA, M. SC.

[Communicated by Dr. R. N. Ghosh, F. N. I., F. A. Sc. (America)]

(Received on June 2, 1949)

INTRODUCTION

Absorption measurements in liquids have generally been made at frequencies ranging from 4 to 15 megacycles where the absorption is fairly large. We have studied the absorption in Benzene, carbon-tetra-chloride, transformer oil and acetic acid at 1·46 and 4 megacycles with the help of an Ultrasonic Interferometer.

It is well known that when elastic waves travel in a liquid medium, an attenuation is produced due to viscosity and heat conduction which has been worked out by Stokes (1845) and Kirchoff (1868). Value of attenuation coefficient ranging from 1500 to 3 times the calculated values have been observed [Willard (1941) Pellam (1946)] in some unassociated liquids in the range from 4 to 15 megacycles but attenuation coefficient is found to be strictly proportional to the square of the frequency in agreement with the formula of Stokes and Kirchoff. In highly viscous liquids Hunter (1941) finds that the observed value of attenuation coefficient is the same as the calculated one.

It may be stated that Stokes and Kirchoff's formula becomes interferomee in the neighbourhood of absorption frequency although tance of the reflector f

it remains true for frequencies much larger than the absorption frequency.

We have verified these results for frequencies 1·46 and 4 Mcs. where the absorption is low and difficult to be measured. Transformer oil which has been studied for the first time is fairly viscous liquid ($\mu = \cdot 051$) and we have been able to verify the results given by Hunter. For Acetic Acid our results agree with those obtained from the theoretical curve of α/N against N, where N is the frequency of the sound wave, given by Pinkerton (1948).

DESCRIPTION AND WORKING OF THE APPARATUS

A quartz plate which is driven by an alternating e.m f. of constant amplitude acts as a source of sound and is placed in the lower portion of a cylindrical vessel in such a way that its radiating face is parallel and opposite to a movable reflector which can be moved by means of a micrometer screw. As the reflector is moved towards or away from the source, the current in the standard circuit to which the crystal plate is connected in parallel shows periodic changes which are easily measurable with a thermocouple meter. At resonance points the meter shows sharp peaks situated one-half acoustic wavelength apart. As the frequency can be determined with the help of hetrodyne wavemeter, the velocity of sound becomes known. The absorption coefficient is determined from the decrement of the reaction.

The chamber wall is a section of brass tubing 1/16" thick, 4" in diameter and 10" high. The crystal support and the micrometer screw with its attached reflector were made a part of the upper plate in order that careful alignment of the crystal and reflector could be made before it was placed in the chamber.

The crystal mounting as shown in (Fig. 1) was designed to hold the crystal in place with a minimum of mechanical friction to its oscillation and to provide an insulated support for leading the r[illegible] frequency driving voltage to the lower surface of the crystal.

The lower electrode which consists of a plane rectangular brass strip rests in a ebonite cavity and soldered to the lead in the middle. The upper electrode is earthed. The whole mounting is provided with three levelling screws to maintain parallelism between upper surface of the crystal and the reflector.

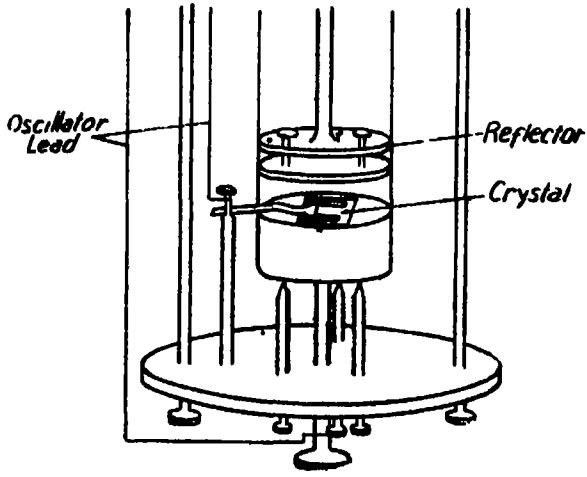


Figure 1

The driving frequency stabilised oscillator, buffer amplifier and the resonance circuits as shown in (Fig. 2) are the standard ones. The oscillator is a frequency stabilised crystal-controlled oscillator. The amplifier is a radio frequency tuned plate amplifier the input of which is coupled to the tank circuit through a condenser of ·001 μfd. The advantage of having a buffer amplifier in between the oscillator and the interferometer is the reduction of the effects of load variations on the frequency of the oscillator. The power at which absorption is to be studied can be studied at will by varying the coupling between the resonance circuit and the output of the amplifier.

A series of observations recording maxima and minima of current for various positions of the reflector as it is moved away from the source are taken. Let $\sigma = (i/I)$ where 'i' is the value of current in the output resonance circuit and I is the maximum value of 'i' at resonance with interferometer disconnected. A curve is plotted between σ and the distance of the reflector from the source. The curve shows a series of

values of σ_{mm} situated one-half acoustic wavelength apart. The attenuation coefficient a may be calculated from the relation given by Fox (1937) between the values of r and σ_{min}

$$ra = \frac{c}{s} \cdot \frac{\sigma_{mm}}{1-\sigma_{mm}} + \text{const}, \qquad (1)$$

where a is the attenuation coefficient and c and s are interferrometer constants which can be determined. Plotting $\sigma_{mm}/(1-\sigma_{mm})$ against r we get a st. line whose slope gives the value of a.

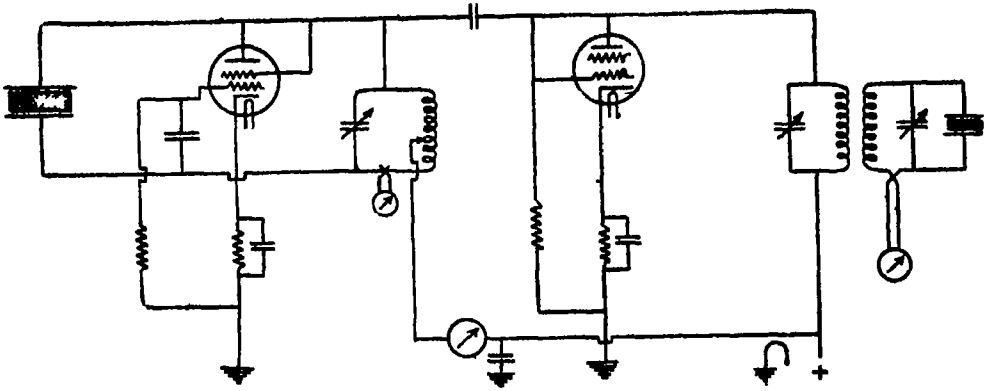


Figure 2

The value of σ_{mm} depends upon the parallelism between crystal and the reflector. It may be argued that since we are measuring very small distances of the order ·005 cm, a lack of parallelism between the crystal and the reflector due to motion of the latter will introduce errors in the value of σ_{mm}, To check the source of error due to this cause we have obtained the values of current for any position of the reflector for serveral independent settings. These are given in Table 1 and it may be seen that the maximum variation in the current does not exceed ·7%. We have therefore taken the mean for several such observations to obtain the value of 'i'. σ_{mm} has been (fig. 3a) obtained by plotting σ (i/I) and r. The minimas are quite sharp. The points on the curve between $\frac{\sigma_{min}}{1-\sigma_{min}}$ and r fall almost on a st. line as shown in Fig. (3b). This also shows that the error due to lack of parallelism

as the reflector is moved is negligible small. Table 1 gives the observations for Benzene.

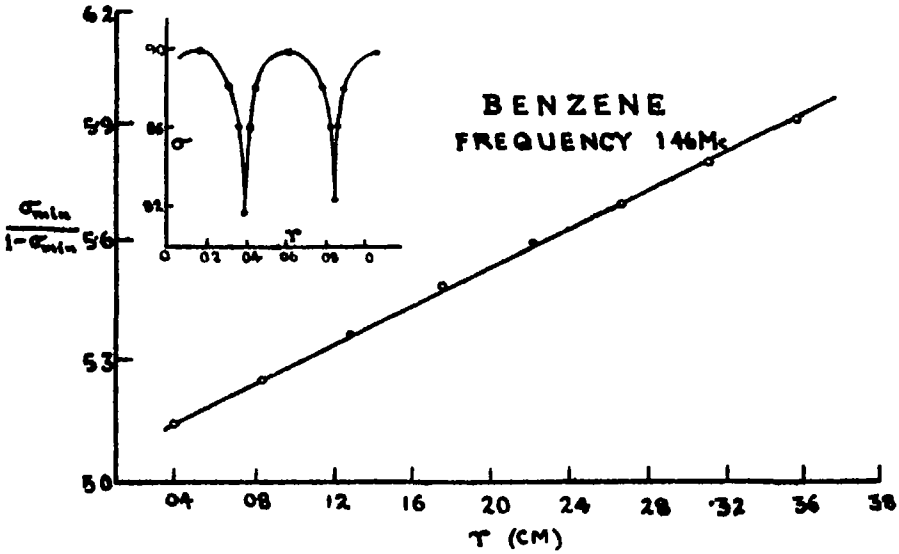


Fig. 3(*a*)

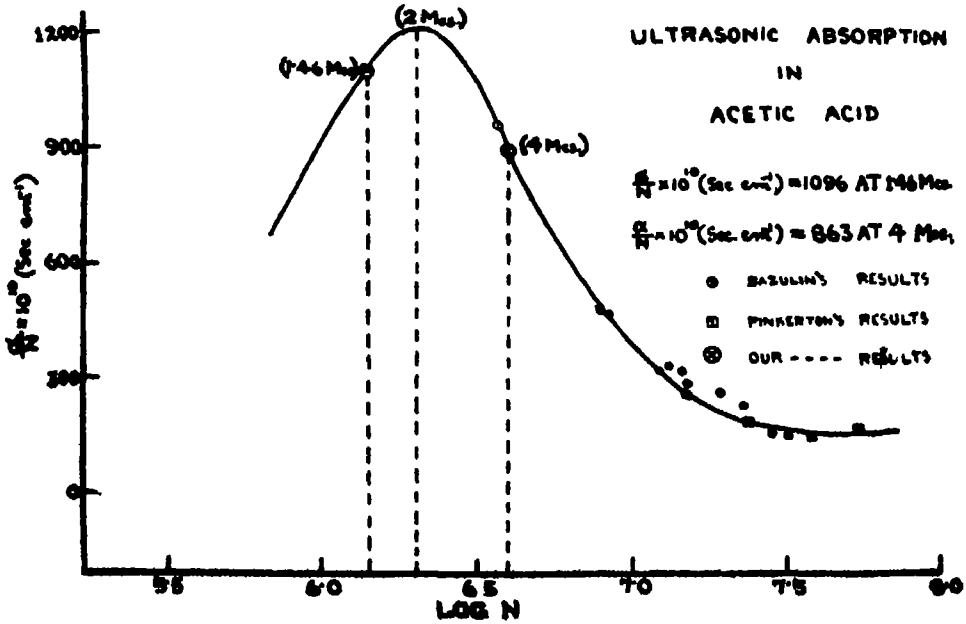


Fig. 3(*b*)

TABLE I

Least count of micrometer screw ·0002 *cm.*

'i' current at minimas

'r' distance of the reflector from the crystal.

r (Cm)	·0400	·0852	·1304	·1757	·2209	·2661	·3113	·3566
'i' 'Ma' a	361	363	366	369	372	374	·377	380
„ 'b'	360	364	366	368	372	375	·377	381
„ c	360	363	367	370	373	375	377	380
„ d	361	364	366	369	373	375	376	381
„ e	360	363	367	369	372	375	377	380
„ f	360	364	366	369	372	375	376	380
Mean	360·3	363·5	366·3	369	372·3	374·8	376·6	380 3
λ/2	226 Div	228 Div	226 Div	226 Div	226 Div	226 Div	226 Div	226 Div

RESULTS AND DISCUSSIONS

The following table shows the values of absorption as well as the velocity of sound waves eperimentally obtained in Benzene, carbon-tetra-chloride, transformer oil and Acetic Acid at 1·46 and 4 Mcs. with the help of formula (1). The wavelength has been measured as the distances between two successive minimas.

TABLE 2

Liquid	Freq.	Temp.	λ Measured	α (Cm^{-1})	$\alpha/N^2 \times 10^{17}$ Sec^2 cm^{-1}	Velocity metre/Sec	Values of α/N^2 obtained by others	Reference
Benzene	1·46Mc.	23°C	·0904 cm	·02	940	1320	923 at 207 Mc.	Gregg (1941)
,,	4 Mcs.	23·2°C	·0905 cm	·15	937	1321	863 at 477 Mcs.	Baumgardt (1937)
Carbon-tetra-chloride	1·46Mc.	23·6°C	·0635 cm	·011	507	928	—	
,,	4 Mcs.	24°C	·0637 cm	·083	520	980	553 at 4·4 Mc	Willard (1941)
Trans-former oil	1·46Mc.	23·4°C	·0879 cm	0021	104	1284		
,,	4 Mcs.	23·2°C	·0880 cm	·0169	106	1286		
Acetic Acid	1·46Mc.	23°C	·0843 cm	·16	7619	1231	extra-polated	Pinketron (1948)
,,	4 Mcs.	23·3°C	·0858	34	2150	1253	2240 at 24 Mc.	Pinkerton (1948)

Benzene has been worked by several workers namely Gregg (1941), Baumgardt (1937). Claeys Errera & Sack (1936), Rieckmann (1939), Bazulin (1937) Lindberg (1940), and Pellam and Galt (1946). The values of $(\alpha/\mathcal{N}) \times 10^{17}$ for Benzene obtained by different workers vary from 800-1157, although a large number of them have found a value in the neighbourhood of 920. As no frquency effect on absorption can be expected at such low frequencies, this difference appears to be due to impurity of Benzene and experimental errors. The values of $\alpha/\mathcal{N}^2$ quoetd in the last column have been chosen because the author worked close to the frequencies used by us.

For carbon-tetra-chloride, Biquard (1935) and Pellam (1946) give a value close to 530 while Willard gives a value of 570 and

Parthasarthy—421, 492. 632. Our value is close to Biquard and Pellam.

Transformer oil has not been worked out previously.

Acetic Acid has been studied by Bazulin (1935-37) and Pinkerton (1948) at several frequencies varying from 4 Mcs. to 15 Mcs. and they have plotted a curve between α/N and log N(Fig. 4) where N is the frequency of the sound wave. The curve is almost a st. line in the region 30 Mcs. to 100 Mcs, the value of $(\alpha/N^2)\times 10^{17}$ being 160. For frequencies below 30 Mcs. t e value shoots up, being 400 at 15 Mcs, 600 at 10 Mcs., 1000 at 7 Mcs., and 2240 at 4 Mcs. They have further extrapolated the curve below 4 Mcs. by using the formula of Kneser (1938) and thus they show that there is an absorption frequency close to 2 Mcs. Our value of $(\alpha/N^2)\times 10^{17}$ at 4 Mcs. agrees with their experimental values as obtained from their experimental curve. The value at 1·46 Mc. obtained by us also agree with the value obtained from their extrapolated curve.

Using the Stokes' and Kirchoff's formula we have calculated the value of $(\alpha/N^2)\times 10^{17}$ for transformer oil. It comes out to be 96 in good agreement with our observed value. This shows that the viscosity effect is most predominant in sound absorption in transformer oil and that the Stoke's formula holds good for viscous substances ($\mu = \cdot 051$)

ACKNOWLEDGEMENT

I offer my sincerest thanks to Dr. R. N. Ghosh, F. N. I., F. A. Sc. (America) for his valuable guidance throughout the progress of the research as well as to Council of Scientific and Industrial Research for a research grant.

References

(1) Stokes, G. G., *Camb. Trans. Phil. Soc.* 82, 87. 1845,
(2) Kirchoff, G., *Pogg. Ann.* 1868, 134, 177.
(3) Willard, G. W., J. A. S. A., 12, 438. 1941,

(4) Pellam & Galt, J. *Chem Phys.* 1946.
(5) Pinkerton. J. M. M., *Nature* vol. 162. 1948.
(6) Fox, P. G., *Phys. Rev.* 52, 973. 1937.
(7) Gregg. E. C., *Jr. Rev. Sci Inst.* 12, 149. 1941.
(8) Baumgardt, E. U., *Compstus Rendus*, 204, 416. 1937.
(9) Claeys, J., Errera. J., Sercle. H., Compstus Rendus., 1936, 202 , 1943.
(10) Rieckmann P., Physik Zeits 40, 582, 1939.
(11) Bazulin P., *Compstus Rendus*, 14, 273, 1937.
(12) Ludberg, P., *Physik Zeits*, 41, 457 , 1940.
(13) Biquard, P., *Doctorate Thesis Paris*, 1935.
(14) Parthasarthy S., *Current Science*, 10, 501, 1938.
(15) Kneser H. O., *Ann. der. Phys.* 32, 281, 1938.

June 2, 1949.

Physics Department
Allahabad University.

THEORY OF THE CLARIONET

By

R. N. GHOSH

Received on September 5, 1949

Some eleven years ago the author published a paper (1) (1938) under the above heading; since then considerable amount of experimental analysis of the tone quality in different registers has appeared. These results combined with Miller's Classical work (2) (1926) have enabled the author to check the theory, and the present paper gives an account of the theoretical work in the light of the experimental work. Considerable light is thrown on the performance of the reed with regard to the tone quality and the presence of even harmonics. We assume as before a uniform of the air chamber, length l, radius a, and neglect radial vibrations in the pipe. We represent the solution of the wave equation for plane waves for excess pressure p by Heaviside's method at any point x measured from the mouth *as*

$$p_x = \eta_1 \sinh \frac{\sigma}{c} x + \eta_2 \cosh \frac{\sigma}{c} x \qquad \ldots \quad (1)$$

where $\sigma = \frac{d}{dt}$; c velocity of sound. The particle velocity u is given by

$$\sigma \rho u = -\frac{dp}{dx}$$

i.e.

$$u = -\frac{1}{c\rho}\left\{\eta_1 \cosh \frac{\sigma}{c} x + \eta_2 \sinh \frac{\sigma}{c} x\right\}.$$

Hence at $x = 0$, $p = \eta_2$, and $u = -\eta_1/c\rho$ $\qquad \ldots \quad (2)$

and,

$$\frac{p_1}{u_1} = -c\rho \left\{ \frac{\eta_1 \sinh \frac{\sigma}{c} l + \eta_2 \cosh \frac{\sigma}{c} l}{\eta_1 \cosh \frac{\sigma}{c} l + \eta_2 \sinh \frac{\sigma}{c} l} \right\}$$

where p_1 and u_1, represent the pressure and particle velocity at $x = l$ the open end. The impedance due to the waves that spread out in the open atmosphere is represented for small values of ka where $k = 2\pi/\lambda$—the where λ is the wave length,

$$Z = c\rho\{R+jX\} \qquad \ldots \quad (4)$$
$$R = k^2a^2/2;\ X = 8ka/3\pi$$

Writing R' for $(R+jX)$ for the sake of brevity we find

$$\frac{\eta_1}{\eta_1} = -\frac{R'\sinh\frac{\sigma}{c}l+\cosh\frac{\sigma}{c}l}{R'\cosh\frac{\sigma}{c}l+\sinh\frac{\sigma}{c}l} \qquad \ldots \quad (5)$$

on equating (3) and (4). The flow velocity u through the chink in the reed will be given by

$$u = K(P-p)(y+y_0) \qquad \ldots \quad (6)$$

where P is the blowing pressure, p the pressure in the month; y_0 represents a permanent displacement of the reed; this represents a permanent opening, and y the varibale displacement measured positively outwards; K—conductivity of the opening. K will have the dimensions of (LT/M), and is supposed to be small. A complete solution of (5) in combination with (6) is very difficult, at the first instance we neglect y in (6) in comparison with y_0 we assume y to be small with respect to y_0, then on substituting the values of p and u from (2) we get

$$-\frac{\eta_1}{K'c\rho} = P-\eta_2, \quad K' = Ky_0$$

And substituting the value of from (5) we get

$$\eta_2 = \frac{P}{\left\{1+\frac{1}{K'c\rho}\,\frac{R'\sinh\frac{\sigma}{c}l+\cosh\frac{\sigma}{c}l}{R'\cosh\frac{\sigma}{c}l+\sinh\frac{\sigma}{c}l}\right\}}$$

This represents Heaviside's solution, and it will be interpreted by the expansion theorem, according to which η_2 will be given by

$$\eta_2 = \frac{Y(0)}{Z(0)}+\sum_{\sigma K}\frac{e^{\sigma k t}}{Z'(\sigma k)}$$

$$Y(0) = 1,\ Z(\sigma) = \left\{1+\frac{1}{K'c\rho}\,\frac{R'\sinh\frac{\sigma}{c}l+\cosh\frac{\sigma}{c}l}{R'\cosh\frac{\sigma}{c}l+\sinh\frac{\sigma}{c}l}\right\}$$

and $\mathcal{Z}'(\sigma_k) = \frac{d\,\mathcal{Z}(\sigma)}{d\sigma}\ \sigma = \sigma_k$, σ_k being the roots of

$$1 + \frac{1}{K'c\rho}\left.\frac{R'\sinh\frac{\sigma}{c}l + \cosh\frac{\sigma}{c}l}{R'\cosh\frac{\sigma}{c}l + \sinh\frac{\sigma}{c}l}\right\}.$$

Two cases arise (1) if K' is large i. e , the mouth is wide open, then we get the imaginary roots

$$\sin\frac{\omega(l+\alpha)}{c} = 0$$

where $\tan\frac{\omega\alpha}{c} = X$, this gives $\omega l'/c \quad m\pi$, where m is any integer, and $l' = (l+\alpha)$.

If K' is small then we find $\cos(\omega l'/c) = 0$

i.e. $\omega l'/c = \frac{m\pi}{2}$, m being an odd integer, and $\lambda_m = 4l/m$.

We write $\qquad R + jX = \beta^2 m^2 + j\alpha m$

$$\beta^2 = \pi^2 a^2/8l^2;\ \alpha = (4a/3l)$$

where a is the radius of the pipe. This holds good for small values of $ka < 1$

$$\frac{\mathcal{Y}(0)}{\mathcal{Z}(0)} = Q(\beta^2 m^2 + j\alpha m)(y' + y)$$

$$y' = (y_0 - AP/Mn^2),\ Q = Kc\rho.$$

Hence $\qquad p = PQ\left[S_0 + (\beta^2 m^2 + \alpha jm)y' + y(\beta^2 m^2 + j\alpha m) + \frac{cy'}{L}\sum\frac{e^{jm\omega_1 t}}{jm\omega_1}\right.$

$$\omega_1 = \pi c/2l' \tag{11}$$

S_0 represents the sum of a finite number of terms in m^2. This sum will have small value. In order to determine y we observe that the equation of motion of the reed

$$(\sigma^2 + n^2)y = \frac{-(P-p)A}{M}$$

where A effective surface of the reed, and M its effective mass $n/2\pi$ redresents its natural frequency.

Hence $\quad y = -\frac{AP}{Mn^2} + \frac{Q_1 cy'}{l}\sum\frac{e^{jm\omega_1 t}}{jm\omega_1(n^2 - m^2\omega_1^2)}$ (12)

where $Q_1 = APQ/M$. substituting this value of y in (11) we get

$$p = PQ\Big[S_1 + \frac{Q_1\beta^2 cy'}{l}\sum\frac{m^2 e^{jm\omega_1 t}}{jm\omega_1(n^2-m^2\omega_1^2)} + \frac{Q_1 acy'}{l\omega_1}\sum\frac{e^{jm\omega_1 t}}{(n^2-m^2\omega_1^2)}$$
$$+\frac{cy'}{l}\sum\frac{e^{jm_1\omega t}}{jm\omega_1} - \text{weak even}$$
$$\text{harmonics} - \frac{Q_1 c^2 y'}{9l^2\omega_1^2}\frac{e^{10j\omega_1 t}}{(n^2-9^2\omega_1^2)}\Big]$$

where it is assumed $n \sim 9\omega_1$, S_1 represents the sum of all the possible terms that are not periodic. The terms containing β^2 may be neglected. Similarly in the cosine series the terms containing $(n^2-m^2\omega_1^2)$, in the denominator where $n \sim m\omega_1$, will be important and have to be retained and the rest may be neglected. Thus finally we shall have

$$p = PQ\Big[S_1 + \frac{acy'}{l\omega_1}\sum\frac{\cos m\omega_1 t}{(n^2-m^2\omega_1^2)} + \frac{cy'}{l}\sum\frac{\sin m\omega_1 t}{m\omega_1}$$
$$-\text{weak even harmonics} - \frac{Q_1 c^2 y'}{9l^2\omega_1^2}\frac{e^{10j\omega_1 t}}{(n^2-9^2\omega_1^2)}\Big]$$

It will be noticed that the coupling of the chink through which air is blown at a constant pressure with the air column is sufficient to maintain the vibration of the air column. In the case of a vibrating reed having a very high natural frequeucy of vibration it does help in the manner expressed by the term $\sum\frac{\cos m\omega_1 t}{(n^2-m^2\omega_1^2)}$. This means that at the initial stage the compressional wave starts with the chink partially widened and when it reaches back after reflection from the open end as rarefaction, the reed has performed four and a half vibration and it has a negative displacement i.e., towards the flat table closing the chink partially, This helps the reflection of the rarefaction from the partially closed end; at this instant the coupling of the mouth piece with the vibrating air column has suddenly altered the pressure to a negative value. When the rarefaction reaches back as compression after reflection from the open end, the reed has performed another four and a half vibration, and at the instant the reed has positive displacement i.e., the chink is widened. The widening of the chink allows more air to enter the mouth piece and the compressional pressure is increased. It will be noticed that the reed performs forced vibration at a frequency $n \sim m\omega_1$, and in order to maintain the

vibration, this condition has to be realised. The reed has only one natural frequency on account of its chiseled shape. In practice the musicians adjust the frequency with care so that the frequency of reed is in agreement with some odd component of the clarionet.

The flow of air is obtained easily from the results that

$$u = \frac{R}{c\rho} p = \frac{\beta^2 m^2}{c\rho} p$$

$$u \sim PQ\left[S_2 + \frac{\beta^2 c y'}{l} \sum \frac{m^2 \cos m\,\omega_1 t}{(n^2 - m^2\omega_1^2)} + \frac{c y'}{l} \sum \frac{m^2 \sin m\omega_1 t}{m\omega_1}\right].$$

Since we sum only upto $m=1$, the summation will not give us infinitely large value It will be noticed that the second term will vanish in the absence of vibration of the reed, and then the coupling term

$$\sum \frac{m^2 \sin m\,\omega_1 t}{m\,\omega_1}$$

will remain and will be sufficient to maintain the vibration of the air column The presence of m^2 in the numerator lends to the belief that the flow velocity series will become divergent i. e. will give a very large value by taking m large Since we sum up to $m=1$ i.e. 6 terms, the presence of the factor β^2 does not allow the summation to obtain infinitely large value for the sum. These results hold good as long as $ka<1$. when $ka \geqslant 1$ then z in (4) will be more complex, and all our formulae will fail to represent the true facts. In actual prectice harmonics up to $m=11$, have been analysed and for pipes of small bore $ka<1$, and then the summatian of the important terms will give a small finite value.

The effect of vibration of the reed is mainly upon the quality of the note. It will be noticed that in the absence of vibration of the need, the pressure changes will practically be given by the sum $\Sigma \sin m\,\omega_1 t/m\,\omega_1$. This summation will give nearly a constant positive pressure with small fluctuations when six or seven terms are considered in the summation viz from m 1 to m 11, over a half cycle, and then suddenly changes to a negative value with similar fluctuations. At the end of the complete cycle, the pressure again rises suddenly

to a positive value. These changes are practically discontinuous. But the vibration of the reed through the terms

$$\sum \frac{\cos m\,\omega_1 t}{(n^2 - m^2\,\omega_1^2)}$$

introduces larger fluctuations of pressure within the half cycle. The near n is to $m\omega_1$, the greater will be the modulations of pressure and hence more of harmonics will elicited near $n \sim m\omega_1$. In general n is larger say $n \sim 9\omega_1$; under these circumstances all those odd components near $9\omega_1$ will be excited. It is possible to fix the value of n by adjusting he vibrating length of the reed, or by slight alteration of the same by the pressure of the lips upon the reed. Thus it will be noticed that player can control the ton quality at pleasure.

The presence of weak even harmonics or a strong component corresponding to the natural frequency of the reed is easily brought about by the product terms which contain an abundance of weak even harmonics. Another point to be noticed is the dependence of the amplitude of the components on Y'

i. e. $(Y_0 - AP/\sqrt{n^2})$

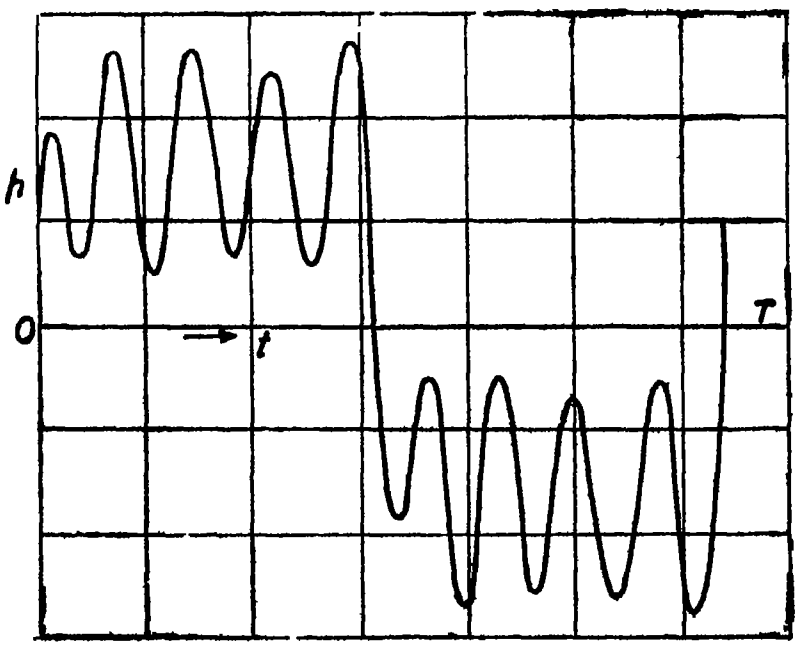


Figure 1

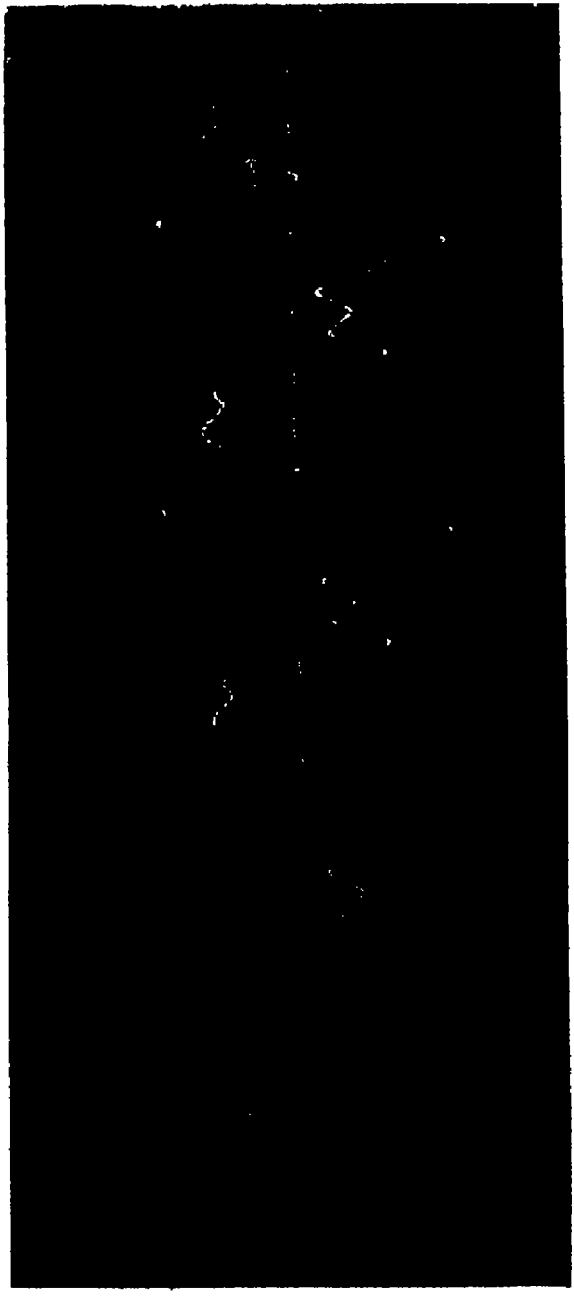


Figure 2

Indian Agricultural Research Institute (Pusa)
LIBRARY, NEW DELHI-110012

This book can be issued on or after _____

Return Date	Return Date